

12.0 EVALUATION OF CHLOROBENZENES

12.1 PHYSICAL AND CHEMICAL PROPERTIES

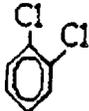
In order to determine which of the 12 chlorinated benzene isomers might pose air pollution problems, we calculated their relative evaporation rates (RERs). The RER, defined as $(0.8217) (\sqrt{\text{molecular weight}})$ (vapor pressure), measures the volatility of various organic compounds relative to n-butyl acetate, which has an RER of 100 (Stratta et al., 1978). Compounds with RERs greater than 1.0 are generally considered volatile, while those with RERs less than 1.0 are usually not volatile.

The chlorobenzene RERs range from 1.5×10^{-4} for hexachlorobenzene to 78.5 for monochlorobenzene. Using this criterion, monochlorobenzene (evaluated in Chapter 9), the three isomers of dichlorobenzene, and the three isomers of trichlorobenzene would all be considered volatile. This judgment is corroborated by Johnston et al. (1979), who state that hexachlorobenzene, pentachlorobenzene, and the isomers of tetrachlorobenzene are not volatile. Therefore, o-, m-, p-dichlorobenzene; 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene might be considered air pollutants because of their potential for emission to the atmosphere. Meta-dichlorobenzene is only produced in trace amounts when monochlorobenzene is chlorinated. The 1,2,3-isomer of trichlorobenzene has relatively few industrial or consumer uses. Because very little of the last two compounds is produced, neither is likely to be emitted to the air in significant quantities.

At normal ambient temperatures, o-dichlorobenzene (o-DCB) is a colorless liquid; p-dichlorobenzene (p-DCB) is a colorless or white crystalline solid; 1,2,4-trichlorobenzene (1,2,4-TCB) is a liquid, and 1,3,5-trichlorobenzene (1,3,5-TCB) is crystalline. Tables 12.1-1 through 12.1-4 summarize some of their physical and chemical properties.

Table 12.1-1

CHEMICAL DATA SUMMARY FOR O-DICHLOROBENZENE

Property	Value for O-Dichlorobenzene
CAS Registry No.	95-50-1
Synonyms	1,2-dichlorobenzene, orthodichlorobenzene, dichlorobenzol
Molecular Weight	147.01
Molecular Formula	$C_6H_4Cl_2$
Molecular Structure	
Physical State at STP	Colorless Liquid
Boiling Point	179°C
Melting Point	-16.7/-18°C
Specific Gravity	
Vapor Pressure	1 mm @ 20°C, 1.5 mm @ 25°C, 1.9 mm @ 30°C
Vapor Density (air=1)	5.07
Solubility	100 mg/L @ 20°C, 145 mg/L @ 25°C
Log Partition Coefficient (octanol/H ₂ O)	3.6
Henry's Law Constant	1.93 atm-L/mole

Source: Verschueren (1977); Johnston et al. (1979), ICF (1985).

Table 12.1-2

CHEMICAL DATA SUMMARY FOR P-DICHLOROBENZENE

Property	Value for p-dichlorobenzene
CAS Registry No.	106-46-7
Synonyms	1,4-dichlorobenzene; Di-chloricide p-Dichlorobenzene; PDB; Paracide; Paradichlorobenzene; p-DCB; p-Dichlorobenzol; Paradichloro- benzol; Parazene; p-Chlorophenyl chloride
Molecular Weight	147.01
Molecular Formula	$C_6H_4Cl_2$
Molecular Structure	
Physical State at STP	Colorless or white crystals
Boiling Point	173.4°C
Melting Point	53°C
Specific Gravity ^a	1.25 g/mL at 20°C
Vapor Pressure	0.6 mm @ 20°C; 1.8 mm @ 30°C
Vapor Density (air=1)	5.07
Solubility	0.079 g/L @ 25°C
Log Partition Coefficient (octanol/H ₂ O) ^a	3.6
Henry's Law Constant ^b	2.89 atm-L/mole

Source: SAI (1980) unless otherwise noted.

^aGrome and Wilkins (1985).

^bICF (1985).

Table 12.1-3

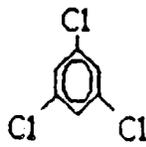
CHEMICAL DATA SUMMARY FOR 1,2,4-TRICHLOROBENZENE

Property	Value for 1,2,4-Trichlorobenzene
CAS Registry No.	120-82-1
Synonyms	asym-trichlorobenzene, 1,2,4-trichlorobenzol, uns-trichlorobenzene
Molecular Weight	181.46
Molecular Formula	$C_6H_3Cl_3$
Molecular Structure	
Physical State at STP	Colorless liquid at STP
Boiling Point	213 ^o C
Melting Point	17 ^o C
Specific Gravity	
Vapor Pressure	0.29 mm @ 25 ^o C
Vapor Density (air=1)	
Solubility	
Log Partition Coefficient (octanol/H ₂ O)	4.3
Henry's Law Constant	2.31 atm-L/mole

Source: Verschueren (1977); Johnston et al. (1979), ICF (1985).

Table 12.1-4

CHEMICAL DATA SUMMARY FOR 1,3,5-TRICHLOROENZENE

Property	Value for 1,3,5-Trichlorobenzene
CAS Registry No.	180-70-3
Synonyms	sym-trichlorobenzene, 1,3,5-trichlorobenzol
Molecular Weight	181.46
Molecular Formula	$C_6H_3Cl_3$
Molecular Structure	
Physical State at STP	White, crystalline solid
Boiling Point	208.5°C
Melting Point	63°C
Specific Gravity	
Vapor Pressure	0.15 mm Hg @ 25°C
Vapor Density (air=1)	
Solubility	
Log Partition Coefficient (octanol/H ₂ O)	
Henry's Law Constant	

Source: Verschueren (1977); Johnston et al. (1979).

Because of their low volatilities, we considered air emissions of tetrachlorobenzene and pentachlorobenzene to be negligible. Furthermore, hexachlorobenzene is a solid at standard temperature and pressure, with very low vapor pressure and RER. Therefore, despite potential sources of air emissions of hexachlorobenzene, which include chlorinated solvent and pesticide production, pesticide application, incineration of certain wastes, landfilling and open disposal of wastes, evaporative losses should be minimal (Thomas, 1985).

12.2 DIRECT PRODUCTION IN CALIFORNIA

As of 1985, there were four production facilities for chlorinated benzenes in the United States. None of these facilities is located in California (Dylewski, 1980; Grome and Wilkins, 1985). The only p-dichlorobenzene (p-DCB) processor identified in California is Specialty Organics Inc., located in Irwindale (SAI, 1980; McAuley, 1985). This company purchases a mixture of dichlorobenzenes and isolates p-DCB for commercial products. The annual production capacity at this plant has been estimated to be 2 million lb each of p-DCB and o-DCB in 1985. Emissions of p-DCB from this plant have been estimated to be about 3.85 tons per year (Grome and Wilkins, 1985).

12.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

According to Grome and Wilkins (1985), p-DCB may be a byproduct of carbon tetrachloride (CCl_4) and perchloroethylene (perc) production. Emissions would occur through distillation column and storage tank vents and various fugitive sources, such as piping. Both carbon tetrachloride and perchloroethylene are produced by Dow Chemical U.S.A. in Pittsburg. To date, however, p-DCB has not been directly measured at any CCl_4 or perc facilities.

Several other forms of indirect production of chlorobenzenes have been documented by Johnston et al. (1979), including the metabolism of the insecticide lindane to various tri- and tetrachlorobenzene isomers by several biological organisms and the degradation of lindane to trichlorobenzene during

the baking of bread and breakfast cereal. The extent and air pollution significance of the generation of these compounds are not known. Lindane is no longer used as a general purpose pesticide, although it may have limited applications.

Studies which have examined wastewater treatment have come to opposite conclusions regarding the production of chlorobenzenes. One study reported that chlorobenzenes were produced during the process, while another stated that they were not (Johnston et al., 1979). Ortho- and para-dichlorobenzene, as well as 1,2,4-TCB, volatilize readily from aerated aqueous solutions (Grome and Wilkins, 1985).

12.4 INDUSTRIAL USE AND EMISSIONS

12.4.1 Ortho-Dichlorobenzene

Ortho-dichlorobenzene is used primarily in the synthesis of organic chemicals. Johnston et al. (1979) cite a 1977 EPA study, which states that 61 percent of all o-DCB produced was employed in organic synthesis, 20 percent was used in the manufacture of toluene diisocyanate, 12 percent for miscellaneous solvents, and 7 percent for other uses. Although toluene diisocyanate is not manufactured in California, it is not known whether the other compounds which use o-DCB are produced here. Ortho-dichlorobenzene is used in conjunction with other solvents as a engine parts cleaner. Other industrial uses for this compound are: coolant for magnetic coils, heat-transfer medium, degreasing agent, and solvent for lacquers and resins.

12.4.2 Para-Dichlorobenzene

About 66 percent of U.S. para-dichlorobenzene production is used to manufacture space deodorants and moth repellants (Grome and Wilkins, 1985). For the former, deodorant manufacturers blend liquid or solid p-DCB with perfumes and other additives and then fabricate dispensers and cakes. Information on California manufacturing of these products was unavailable. Use of deodorants and moth repellants is discussed in Section 12.5.

Another 24 percent of U.S. para-dichlorobenzene production is used as a reactant in the production of polyphenylene sulfide (PPS) resin. There appear to be no PPS manufacturing facilities in the state (Johnston et al., 1979; Grome and Wilkins, 1985).

The remaining p-DCB is used as a dye intermediate, as a feedstock for insecticides, and directly as a general insecticide and soil fumigant. The breakdown for these categories is unknown. No manufacturers of para-dichlorobenzene-based dyes in California have been identified. Only one pesticide, chlorfenethol, has been identified in the literature as being a p-DCB derivative (Sittig, 1980). Methoxychlor, which may be manufactured from para-dichlorobenzene, is produced by Kincaid Enterprises, Inc. and Lee Chemical Company in Fillmore (Grome and Wilkins, 1985).

12.4.3 Trichlorobenzenes

Two of the trichlorobenzene isomers (1,2,4-TCB and 1,3,5-TCB) have important industrial uses. 1,2,4-TCB, the more important compound, is used as a dye carrier; a solvent for fats, oil, waxes, resins; a degreasing solvent; dielectric fluid; lubricating oil additive; and glass tempering additive. The pesticides Dicamba, Tecnazene, and Tetradifon are also manufactured using this isomer. Finally, this compound can be used as a coolant in electrical installations.

Approximately 46 percent of the trichlorobenzenes produced are used as dye carriers, and 28 percent as herbicide intermediates. Which of the above industrial uses for TCB occur in California is not presently known.

12.5 CONSUMER USES AND EMISSIONS

The primary uses of o-dichlorobenzene are industrial. However, o-DCB does find its way into consumer items through its use as a solvent for lacquers. On the other hand, p-dichlorobenzene is widely used in consumer items. About 44 percent of the annual U.S. use of this isomer is as a constituent of space deodorants; another 22 percent is used in moth control

blocks. Something less than 10 percent is used in insecticides.

A recent study for the U.S. Environmental Protection Agency's Pollutant Assessment Branch estimated that 23,000 MT of p-dichlorobenzene were used nationally in 1983 as space deodorants and moth repellants (Grome and Wilkins, 1985). Assuming that all of the p-DCB volatilizes and that California's population is 11 percent of U.S. population, we estimate 1983 p-DCB emissions from this source to be $(0.11) (23,000 \times 10^6 \text{ g}) (1\text{b}/453.6 \text{ g})$ (ton/2000 lb) = 2,790 tons (2,530 MT). Since total p-DCB production increased by 4.7 percent between 1983 and 1985, emissions from space deodorant and moth repellent use in 1985 would be $(2,790 \text{ tons})(1.047) = 2,920 \text{ tons} (2,650 \text{ MT})$.

Para-dichlorobenzene is used directly as a general insecticide and soil fumigant, marketed under the trade name Paracide (Grome and Wilkins, 1985). The extent of this use is unknown.

12.6 EMISSIONS SUMMARY

None of the chlorobenzenes reviewed in this study is manufactured in California, although p-DCB is isolated at one plant from a crude mixture of dichlorobenzenes; emissions from this facility are estimated to be 3.85 tons per year. A potential indirect emission source is byproduct formation during manufacture of carbon tetrachloride and/or perchlorethylene at one plant in the state. Chlorination of drinking water is not a significant source of chlorinated benzenes. Formation of chlorobenzenes during wastewater treatment has been reported in the literature, but has not been confirmed in recent studies. Finally, various chlorobenzenes may be products of metabolism and degradation of the insecticide lindane.

There is no evidence that o-dichlorobenzene is used in California as a feedstock, although it is possible that it is used industrially as a coolant for magnetic coils, heat transfer medium, degreasing agent and solvent. Para-dichlorobenzene is used as a feedstock for the pesticide chlorfenethol and may be used in methoxychlor. Whether it is used this way in California is unknown. Para-dichlorobenzene has several other industrial uses, but none

appears to be significant in California. The two trichlorobenzenes investigated are also used industrially as pesticide intermediates and solvents, but we could find no information on the extent of their use in the state.

Para-dichlorobenzene is a major constituent of moth control blocks and room deodorants. California emissions from these consumer products are estimated to be 3,000 tons per year.

12.7 SUMMARY OF AMBIENT CONCENTRATION DATA

12.7.1 Gas Phase Concentrations

A number of measurements have been made of ambient levels (including near-source) of dichlorobenzenes and their higher homologues. As noted in Section 9.7.1 for monochlorobenzene, the available data base may contain discrepancies. Concentrations are available for the three dichlorobenzene isomers (Table 12.7-1). However, no data are available for p-dichlorobenzene in California. Mean values for the ortho and meta isomers at California sites are in the range 4 - 130 ppt.

Concentration data for trichlorobenzenes and tetrachlorobenzenes are presented in Table 12.7-2. Mean trichlorobenzene values at California locations are in the range 3 - 10 ppt. A single sample collected at Torrance yielded a value of 360 ppt. There are no data for tetrachlorobenzene in California or elsewhere, with the exception of a few samples collected in and near Henderson, NV, where industrial emissions include both chlorine and aromatic hydrocarbons. No data on ambient levels of pentachlorobenzene were found in the literature. Hexachlorobenzene levels of 0.05 - 0.11 ng/m³ have been measured in ambient Portland, OR air (Ligocki et al., 1985).

Table 12.7-1

AMBIENT CONCENTRATIONS OF DICHLOROBENZENES
(Concentrations in ppt)

Compound	Location	Concentration		Reference
		Mean	Maximum	
ortho (1,2-dichloro)	Los Angeles, CA	130	310	a
	Oakland, CA	40	60	a
	Riverside, CA	10	16	a
	Upland, CA	13	67	b
	Other U.S. locations:			
	urban	56	660	a
near-source	200	2,200	a	
meta (1,3-dichloro)	Los Angeles, CA	77	150	a
	Oakland, CA	65	96	a
	Riverside, CA	4	9	a
	Other U.S. locations:			
	urban	83	2600	a
	near-source	150	740	a
para (1,4-dichloro)	California locations	No data	No data	a
	Other U.S. locations:			
	urban	290	10,000	a
	near-source	2.6	11	a
All three dichloro- benzene isomers	Delft, Vlaardingen and Terschelling, The Netherlands	60-100	730-2,500	c

^aBrodzinski and Singh, 1983.

^bPellizzari, 1979.

^cGuicherit and Schulting, 1985.

Table 12.7-2

AMBIENT CONCENTRATIONS OF TRICHLORO-, TETRACHLORO-,
PENTACHLORO- AND HEXACHLOROBENZENE
(Concentrations in ppt)

Compound	Location	Concentration		Reference
		Mean	Maximum	
<u>Trichlorobenzene</u>				
1,2,4-isomer	Los Angeles, CA	7	34	a
	Oakland, CA	3	15	a
Isomer not specified (probably 1,2,4)	Los Angeles, CA	7	14	b
	Oakland, CA	3	8	b
	Riverside, CA	10	12	b
	Torrance, CA	360	360	c
Sum of 3 isomers (1,2,3 + 1,2,4 + 1,3,5)	Delft, Vlaardingen The Netherlands	10-20	40-1350	d
<u>Tetrachlorobenzene</u>				
	California	No data	-	
	Other U.S. Locations:			
	urban	690	690	e
	near-source	95	95	e
<u>Pentachlorobenzene</u>				
	California	No data	-	
	Elsewhere	No data	-	
<u>Hexachlorobenzene</u>				
	California	No data	-	
	Portland, OR	0.015	0.020	f

^aSingh et al., 1981.

^bBrodzinsky and Singh, 1983.

^cPellizzari, 1977.

^dGuicherit and Schulting, 1985.

^eWojinski et al., 1979.

^fLigocki et al., 1985.

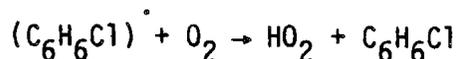
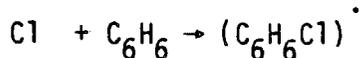
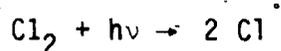
12.7.2 Condensed Phase Concentrations

No data are available for chlorobenzenes (from dichloro to hexachloro) in California fog, rain, or aerosol samples. Ligocki et al. (1985) measured chlorobenzenes in seven rainwater samples collected in Portland, OR. They identified 1,2-dichlorobenzene (0.13 - 0.62 ng/L), 1,4-dichlorobenzene (3.0 - 7.0 ng/L) and 1,2,4-trichlorobenzene (0.13 - 0.45 ng/L).

12.8 ATMOSPHERIC CHEMISTRY

12.8.1 In-Situ Formation

As discussed in Section 9.8.1 for monochlorobenzene, in-situ formation of chlorobenzenes would require reaction of chlorine atoms with benzene, e.g.:



followed by reaction of chlorobenzene with Cl to yield dichlorobenzenes, and so on. This reaction, while perhaps of importance in near-source areas impacted by emissions of chlorine and benzene, is probably of negligible importance in urban air.

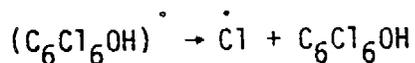
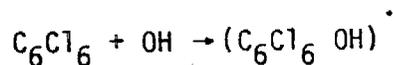
12.8.2 Removal Processes

Reactions of chlorobenzenes with ozone and with the nitrate radical are of negligible importance in the atmosphere. The importance of photolysis as a removal process may increase with the number of chlorine atoms attached to the aromatic ring, but no experimental data are available regarding photolysis of chlorobenzenes in sunlight. All chlorobenzenes appear to react, albeit slowly, with the hydroxyl radical. Recent data of Davenport et al.

(1986) and of Zetzch et al. (as cited by Dilling et al., 1986) are as follows:

Chlorobenzene	$k_{OH}, \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$
monochloro	9.5×10^{-13}
o-dichloro	4.2×10^{-13}
m-dichloro	7.2×10^{-13}
p-dichloro	3.3×10^{-13}
1,2,4-trichloro	5.5×10^{-13}
tetra, penta, hexachloro	No data

Thus, it appears that chlorobenzenes, if not removed by photolysis (for which no data exist), may be long-lived atmospheric contaminants. Their slow reaction with OH is assumed to proceed, as for other aromatic hydrocarbons, by addition on the aromatic ring, with the site of OH attack reflecting the ortho-para orientation effect of the chlorine atoms. The OH-chlorobenzene adduct is expected to react with NO_2 to form nitrochlorobenzenes, with O_2 (abstraction) to form chlorophenols, and with O_2 (addition) to form, upon aromatic ring opening, chlorinated aliphatic dicarbonyls. These, in turn, are expected to be rapidly removed by photolysis and by reaction with OH. Tentative reaction mechanisms that summarize these pathways are given in Figure 12.8-1 for p-dichlorobenzene and in Figure 12.8-2 for 1,2,4-trichlorobenzene. The reaction of hexachlorobenzene with OH, which of necessity involves OH addition on a chlorine-bearing carbon atom, may involve different pathways, including elimination of a chlorine atom from the adduct, e.g.:



to yield pentachlorophenol, $\text{C}_6\text{Cl}_5\text{OH}$.

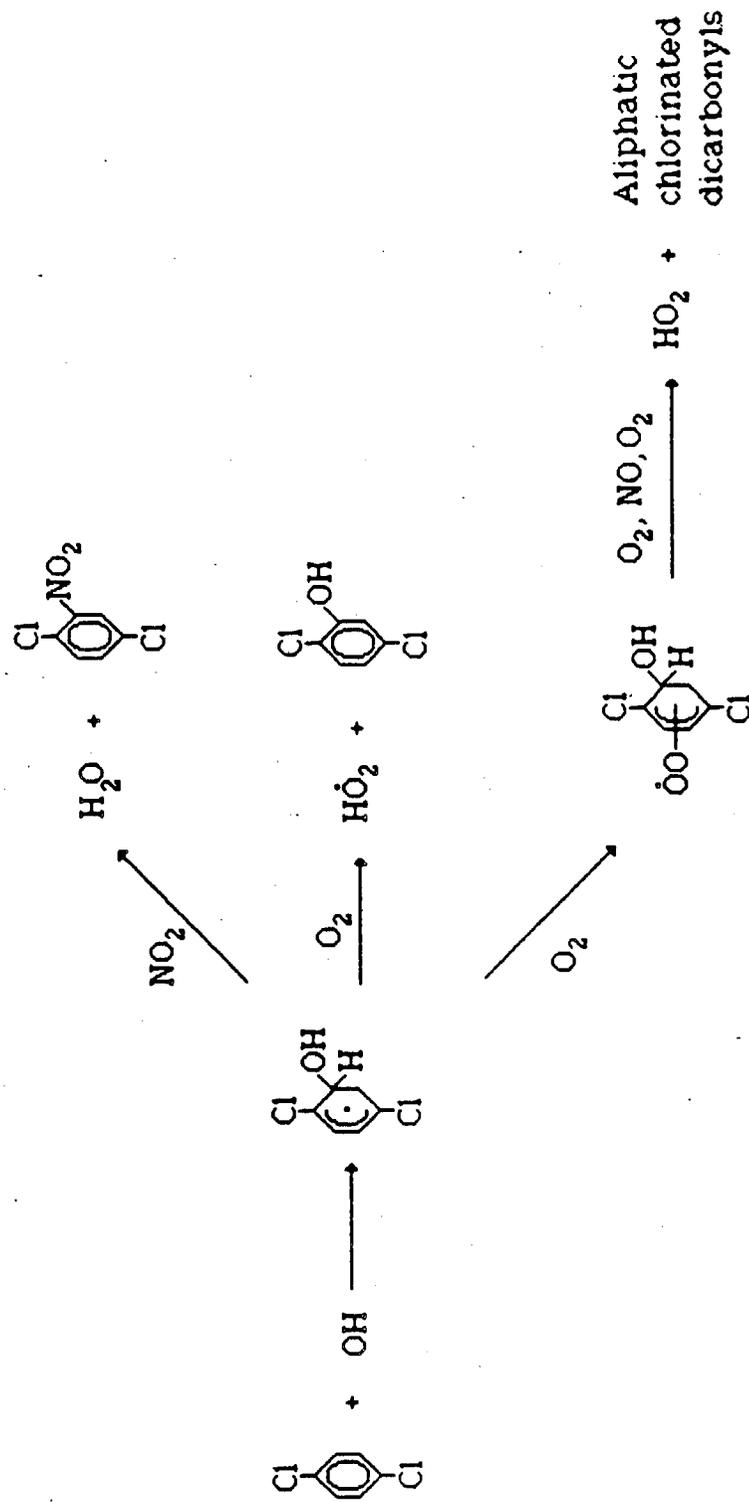


Figure 12.8-1. Reaction of OH With p-Dichlorobenzene.

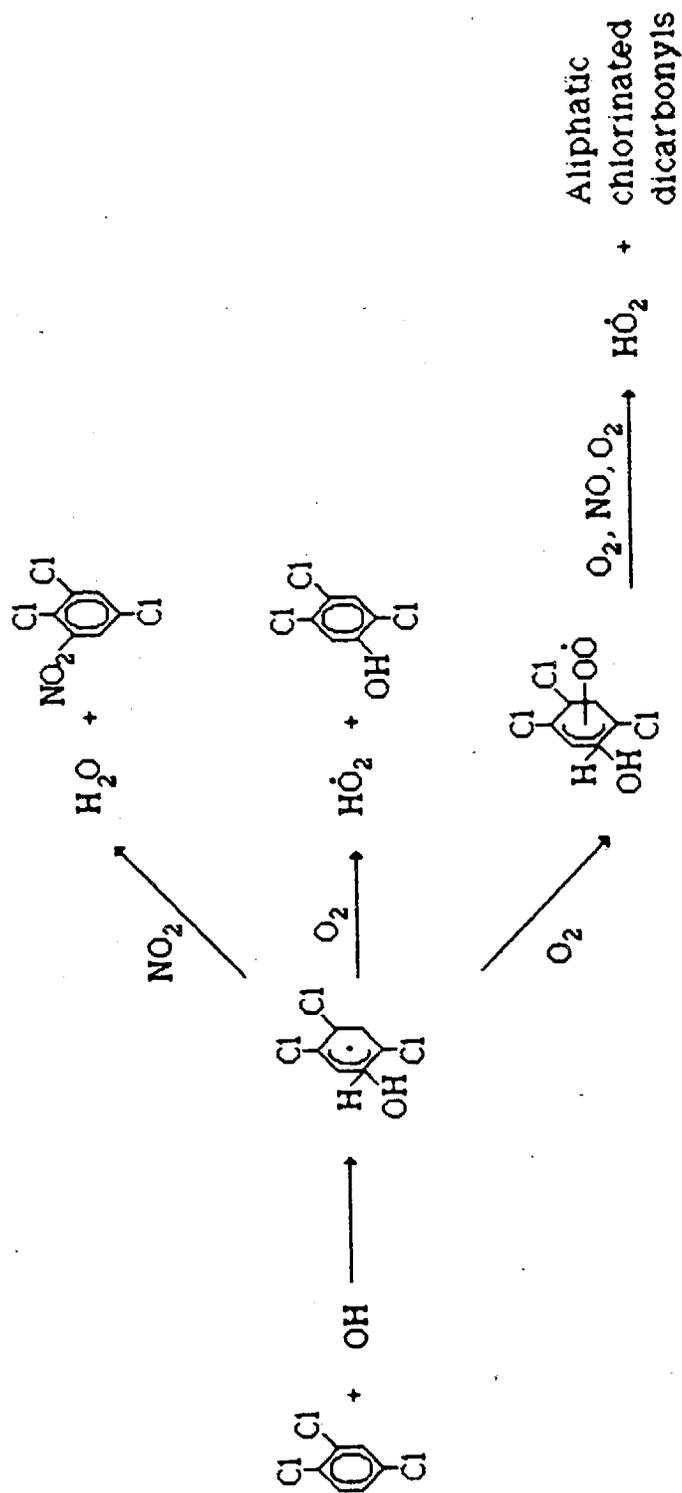


Figure 12.8-2. Reaction of OH With 1,2,4-Trichlorobenzene.

12.9 REFERENCES

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13.0
EVALUATION OF DIALKYL NITROSAMINES

13.1 PHYSICAL AND CHEMICAL PROPERTIES

This study has focused upon the three most volatile dialkyl nitrosamines, N-dimethylnitrosamine (DMN), N-diethylnitrosamine (DEN), and N-methylethylnitrosamine (MEN): DMN is a yellow oily liquid of low viscosity. Table 13.1-1 summarizes some of its physical and chemical properties. DEN is a yellow volatile liquid. Table 13.1-2 summarizes some of its physical and chemical properties. Data on the properties of MEN were unavailable.

13.2 DIRECT PRODUCTION IN CALIFORNIA

None of the nitrosamines under consideration in this chapter is presently produced commercially in the U.S. (SRI, 1979; 1982).

13.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

As will be discussed in Sections 13.5 and 13.6, use of dialkyl nitrosamines in California in industrial processes and consumer products is probably negligible. Other sources must therefore account for observed atmospheric concentrations. Since nitrosamines are known to form in the atmosphere from secondary and tertiary amines, our review focused upon both stationary and mobile sources of these precursors.

13.3.1 Stationary Sources

To the best of our knowledge, amines are not manufactured in California. However, amines are released from a variety of activities, and dialkyl nitrosamine formation has been associated with some of them. For example, dimethylamine and various secondary and tertiary amines have been identified in air samples taken near feedlots (Roberts, 1980).

Table 13.1-1
CHEMICAL DATA SUMMARY FOR N-NITROSODIMETHYLAMINE

Property	Value for N-nitrosodimethylamine
CAS Registry No.	62-75-9
Synonyms	N-dimethylnitrosoamine; nitrous dimethylamide
Molecular Weight	74.08
Molecular Formula	$(\text{CH}_3)_2\text{NNO}$
Molecular Structure	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{N} - \text{NO} \\ \diagup \\ \text{CH}_3 \end{array}$
Physical State at STP	Yellow oily liquid
Boiling Point	152/153°C
Melting Point	
Specific Gravity	
Vapor Pressure	
Vapor Density (air=1)	2.56
Solubility	
Log Partition Coefficient (octanol/H ₂ O)	
Henry's Law Constant	

Source: SAI (1980).

Table 13.1-2
CHEMICAL DATA SUMMARY FOR N-NITROSODIETHYLAMINE

Property	Value for N-nitrosodiethylamine
CAS Registry No.	55-18-5
Synonyms	N-nitrosodiethylamine; diethyl-nitrosamine; nitrous diethylamide
Molecular Weight	102.14
Molecular Formula	$(C_2H_5)_2NNO$
Molecular Structure	$ \begin{array}{c} C_2H_5 \\ \diagdown \\ N - NO \\ \diagup \\ C_2H_5 \end{array} $
Physical State at STP	yellow liquid
Boiling Point	177°C
Melting Point	
Specific Gravity	
Vapor Pressure	
Vapor Density (air=1)	
Solubility	
Log Partition Coefficient (octanol/H ₂ O)	
Henry's Law Constant	

Source: SAI (1980).

Dimethylnitrosamine has also been observed in these settings. Possible pathways to nitrosamine formation in feedlots include (1) reaction of amines with nitrite in wastes and (2) atmospheric reaction of feedlot amines with NO_x (USEPA, 1977).

DMN has also been reported in workspace air in leather tanneries, where dimethylamine is used as an accelerator in the liming process (Ember, 1980). California has about 30 leather tanneries (USDOC, 1981).

DMN, DEN and MEN have been measured in both mainstream and sidestream smoke from cigarettes and cigars. Using data summarized by Fine (1980), and an estimate of 6.53×10^{10} cigarettes smoked per year in California (see Section 4.3.5), we estimate total emissions of 120 to 1,000 lb/yr from this source. About 97 percent of these emissions are as dimethylnitrosamine.

Various amines have been found in digester exhaust gases at animal rendering plants, including glue factories. However, emission controls which treat odorous vapors from these plants remove over 99.9 percent of the potential amine emissions (Roberts, 1980).

Secondary and tertiary amino compounds used as pesticides and herbicides have been found to react with nitrite to form N-nitroso compounds. A mid-1970s investigation of commercial weed killers found DMN concentrations from 0.3 mg DMN/liter in a home lawn-care product to 640 mg DMN/liter in an industrial herbicide (USEPA, 1977). Examples of agricultural chemicals which form DMN in in-vivo and in-vitro reactions in the presence of nitrite are dimethyldithiocarbamate (ziram) and iron dimethyldithiocarbamate (ferbam). In 1984, about 817,500 lb of ziram and 17,200 lb of ferbam were applied by licensed applicators in California (Gatenby, 1986). The amount in general agricultural use is unknown. Data for estimating potential DMN emissions are insufficient.

Other uses of amines which could potentially result in the release of dialkyl nitrosamine precursors to the atmosphere include preparation of rubber

vulcanization accelerators, pharmaceuticals, herbicides, fungicides, and insecticides. Triethanolamine is present at up to 40 percent in synthetic cutting fluids (Fine, 1980). Dimethylamine is also used, along with methylformate, to produce dimethyl formamide. The extent of amine emissions from these activities in California is unknown at this writing.

13.3.2 Mobile Sources

In the 1970s a number of studies examined the exhaust gases of gasoline-powered and diesel-powered automobiles for traces of nitrosamines and amines. Some of these looked at the effect of gasoline additives and emission control systems on emissions. Despite extreme caution in sampling and analytic techniques, because of the unstable nature of N-nitroso compounds, no evidence was found for either amine or nitrosamine emissions from any tested sources (USEPA, 1977). Later work conducted at the U.S. Bureau of Mines, using more sensitive detection techniques, particularly electrolytic conductivity, allowed researchers to lower detection limits to about 25 ppb for nitrosamines. In one experiment, automobile exhaust samples in light-proof bags were spiked with known concentrations of ammonia, alkyl and aryl amines, nitrites, and nitrosamines to several times their detection limits. After 30 minutes less than 30 percent of the original amounts remained, indicating that these compounds are unstable and undetectable in auto exhaust (USEPA, 1977).

Slone et al. (1980) used Tenax-GC adsorbent traps to sample for DMN in diesel exhaust and blowby at selected modes of a 13-mode cycle. The limits of detection were 90 and 10 ppt for the exhaust and blowby respectively. No DMN was detected.

Cadle and Mulawa (1980) sampled exhaust gas concentrations of ammonia and three amines from 17 mid-1970s automobiles tested on a dynamometer, using the 1975 Federal Test Procedure. Dimethylamine (DMA) and diethylamine (DEA) were present in many, but not all, of the samples, while triethylamine (TEA) was not detected. DMA and DEA averaged 20 and 18 ppb, respectively, in

undiluted exhaust. An emission rate of about 0.1 mg/mile was estimated for DEA. Cadle and Mulawa conclude that, given rapid dilution of these emissions and slow reaction rates for nitrosation, resulting nitrosamine concentrations would be in the sub part-per-trillion range at night. Concentrations would be lower during the day, because nitrosamines photolyze in sunlight (see Section 13.8.2). Automobile emissions would therefore not be expected to be responsible for a significant fraction of the nitrosamine concentrations observed in urban areas. (See Section 13.7.1)

In experiments conducted by Smith and Black (1980), four 1978 and 1979 model cars equipped with three-way catalysts were tested over four driving cycles, using three types of fuel. Diethylamine and triethylamine emissions were below their detection limits (0.1 - 1.0 mg/mile and 0.13 - 1.4 mg/mile, respectively, depending upon the driving cycle). DMA could not be distinguished from monoethylamine (MEA) emissions by the analytical procedures used. Combined DMA and MEA emissions were below the minimum detectable value (0.05 - 0.63 mg/mile, depending upon the driving cycle).

Pierson and Brachaczek (1983), after reviewing these and other studies of amine and nitrosamine emissions, conclude that "the amount of nitrosamines emitted in automobile exhaust is inconsequential," and that dialkylamines are definitely not emitted "at rates sufficient to form significant amounts of nitrosamines by reactions in the atmosphere with traces of nitrous oxide or even concurrently emitted nitrogen oxides." Subsequent tests by these researchers of ambient alkylamine concentrations in a highway tunnel led to the same conclusion about on-road emissions from both gasoline- and diesel-powered vehicles. DMA, DEA, and TEA emissions were all below the detection limit of 0.06 - 0.5 mg/mile for gasoline vehicles and 0.13 - 1.1 mg/mile for heavy-duty diesels.

13.4 INDUSTRIAL USE AND EMISSIONS

Although numerous potential industrial uses exist for the three nitrosamines of interest and patents for these uses have been obtained, it

does not appear as if the compounds have been widely used (USEPA, 1977). to the best of our knowledge the only industrial use of a dialkyl nitrosamine in California has been as a feedstock for the rocket fuel 1,1-dimethylhydrazine. The Teledyne-McCormick-Selph facility in Hollister used DMN to manufacture fuel; production ceased in 1978 (Roberts, 1980). Other uses for DMN are industrial solvent, antioxidant, and solvent in the fiber and plastics industry. This compound has also been used in lubricants, condensers, and as a nematocide. Many, if not most, of these uses have been discontinued because of concern over the carcinogenicity of nitrosamines (IARC, 1972-present; USEPA, 1977). DEN has been used as a gasoline and lubricant additive, antioxidant, and stabilizer (IARC, 1972-present). MEN has been used only as a research chemical. Synthetic cutting fluids, semisynthetic cutting oils, and soluble cutting oils may contain nitrosamines, either as contaminants in amines, or as products from reactions between amines and nitrite. Nitrosamine concentrations ranging from 1 to 1,000 ppm have been found in certain of these oils (Sittig, 1981).

13.5 CONSUMER USE AND EMISSIONS

We were unable to find much information on actual DEN use in industrial consumer formulations. A number of nitrosamines have been patented for use as gasoline and lubricant additives, antioxidants, and also pesticides.

The previous discussion indicates that nitrosamines, in particular DMN and DEN, have been found in a variety of consumer products. Since these compounds are volatile, a certain proportion will be emitted to the atmosphere. We are not aware of attempts to perform mass balance calculations or to assess the amount of DMN, DEN, or MEN produced in the air of a closed system containing any of the products. It is, therefore, not possible to estimate actual emissions of these nitrosamines in California due to use of consumer products.

13.6 EMISSION SUMMARY

None of the three dialkyl nitrosamine compounds of interest is produced in California. Nitrosamines may form in the atmosphere from reactions with secondary and tertiary amines. They have been found in some industrial processes, high explosives, livestock and poultry manure, animal rendering plants, and leather tanneries. Amine precursors are used in the preparation of rubber accelerators, pharmaceuticals, herbicides, fungicides, and insecticides, and in the leather tanning industry. DMN is used as an industrial solvent, antioxidant, solvent in the fiber and plastics industry, and in lubricants and condensers. DEN has been used as a gasoline and lubricant additive. The extent of any of these activities in California is unknown as of this writing. The amounts of dialkyl nitrosamines emitted to the atmosphere and formed in-situ are not presently known.

13.7 SUMMARY OF AMBIENT CONCENTRATION DATA

13.7.1 Gas Phase Concentrations

Concern about the toxicity of nitrosamines reached a peak in the mid-1970s and prompted a number of studies of their environmental concentrations (e.g. reviews of Fine et al., 1979; Fine, 1980). Since that time, interest in nitrosamines has decreased considerably, even though substantial uncertainties remain concerning the environmental fate of these compounds, their concentrations in ambient air, and the chemistry of their formation and removal in the atmosphere.

Of the three dialkyl nitrosamines under consideration in this chapter, only one, dimethylnitrosamine, $(\text{CH}_3)_2\text{NNO}$, has been measured in ambient or near-source air. No data are available for diethylnitrosamine, $(\text{C}_2\text{H}_5)_2\text{NNO}$, methyl-ethyl nitrosamine, $\text{C}_2\text{H}_5\text{N}-\text{CH}_3$, or other dialkyl nitrosamines.

NO

Bretschneider and Matz (1974) first reported on airborne dimethyl

nitrosamine at an amine factory in Germany. Concentrations were in the range 1-430 ppt. Subsequent studies carried out in the United States focused on industrial sites, e.g. those producing dimethylhydrazine and secondary amines. Results of these studies are summarized in Table 13.7-1. Reported concentrations varied widely, from below detectable levels (of a few ppt) to levels as high as 10 ppb.

Only two studies have been conducted at California locations. Pellizzari (1977) found no dimethyl nitrosamine in samples collected in Los Angeles. Gordon (1978) monitored dimethylnitrosamine in Contra Costa County (20-360 ppt) and at 15 locations in the Los Angeles area (average 1-31 ppt, maxima up to 160 ppt; see details in Table 13.7-1).

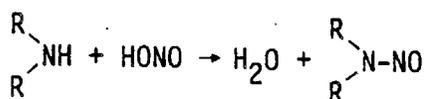
13.7.2 Condensed Phase Concentrations

There are no data regarding dimethyl, diethyl, and methyl ethyl nitrosamine in fog, rain and aerosol samples, in California or elsewhere.

13.8 ATMOSPHERIC CHEMISTRY

13.8.1 In-Situ Formation

Nitrosamines may form in the atmosphere from secondary and tertiary amines according to two reactions. The first reaction involves nitrosation of amines in the dark (at night) by reaction with nitrous acid, e.g.:



The second reaction involves the OH-initiated photooxidation of secondary and tertiary amines. As will be discussed later in this section, this second reaction, which constitutes a daytime pathway for nitrosamine formation, is compensated by rapid removal of nitrosamines due to their photolysis in sunlight.

Table 13.7-1
 AMBIENT LEVELS OF DIMETHYLNITROSAMINE
 (Concentrations in ppt^a)

Location	Concentration	Reference
Amine plant in Germany	1-430	Bretschneider and Matz, 1974
Philadelphia, PA	25	Fine et al., 1976
Baltimore, MD	22-960	
Belle, TX	14-51	
Baltimore, MD	140-10,670	Pellizzari et al., 1976
Baltimore, MD	11-1,000	Fine et al., 1977
Baltimore, MD ^b	5-253	
Los Angeles, CA ^c	None detected	Pellizzari, 1977
Contra Costa Co.	20-360	Gordon, 1978
Los Angeles area ^d		
Burbank	9.2 (160), 47/156	
Compton	0 (0), 0/10	
Hollywood	3.3 (27), 1/10	
Huntington Park	8.3 (60), 5/18	
Long Beach	14 (130), 7/19	
Los Angeles	2.3 (37), 1/15	
Palos Verdes	14 (53), 5/13	
Pasadena	31 (67), 6/7	
Pomona	4.3 (43), 3/13	
San Fernando	17 (113), 3/8	
San Gabriel Mountains	6.3 (47), 2/9	
Santa Monica	9 (47), 4/13	
Torrance	1.7 (17), 3/13	
Whittier	5.6 (53), 2/12	
Woodland Hills	5.3 (27), 2/8	

^a Conversion factor for dimethylnitrosamine: 1 ppt = 3 ng/m³.

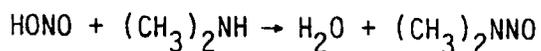
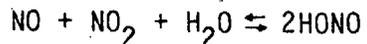
^b 28 urban sites.

^c 15th and Emery Street.

^d Average, (maximum), number of detectable observations/total number of samples.

13.8.1.1 Dark Reaction of Amines With Nitrous Acid

Hanst et al. (1977) investigated the reaction of dimethylamine, NO and NO₂ in dry nitrogen. The amine loss was negligible (1 percent per minute, probably by diffusion to the reactor walls) and no dimethylnitrosamine formed. Nitrosamine formation by direct reaction of NO or NO₂ with amines can be therefore ruled out. In contrast, dimethyl amine reacted readily in the dark with a mixture of NO and NO₂ in humid air (H₂O = 13,000 ppm) to form dimethylnitrosamine (Hanst et al., 1977). Nitrosamine thus forms by reaction of the amine with nitrous acid, which forms in the dark by reaction of oxides of nitrogen with water vapor:



Nitrosamine formation from amine-NO_x mixtures in humid air in the dark has been observed for four amines: dimethyl, diethyl, trimethyl and triethyl (Hanst et al., 1977; Grosjean et al., 1977; Pitts et al., 1978, Tuazon et al., 1978). Dimethylnitrosamine is formed from the methyl amines, and diethylnitrosamine from the ethyl amines. Formation of nitrosamines from secondary amines is as shown above. The mechanism of nitrosamine formation from tertiary amines has not been firmly established. Methyl ethyl nitrosamine has not been studied experimentally. It is expected to form from methyl ethyl amine and from any tertiary amine that contains at least one methyl and one ethyl group, e.g. C₂H₅N(CH₃)₂, (C₂H₅)₂NCH₃, C₂H₅N(R)CH₃.

Nitrosamine yields in the above studies were low and varied as expected with precursor concentrations. The $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HONO}$ equilibrium constant is about $1.6 \times 10^{-6} \text{ ppm}^{-1}$ (Hanst et al., 1977). In the study of Hanst et al., involving 1 ppm dimethylamine, 2 ppm each NO and NO₂ and 13,000 ppm H₂O, the HONO concentration was 0.5 ppm and the (CH₃)₂NNO yield was 10-30 percent. The experiments of Pitts et al. (1978) involved 0.5 ppm amine, 0.08 ppm NO and 0.16 ppm NO₂ at relative humidities of 25-50 percent.

Nitrosamine yields were substantially lower than those of Hanst et al. (1977), since much less HONO₂ formed from the lower NO_x concentrations: 2.8 percent for diethylnitrosamine from diethylamine, 0.8 percent for diethylnitrosamine from triethylamine, 1 percent for dimethyl nitrosamine from dimethylamine, and trace amounts of dimethylnitrosamine from trimethylamine.

The importance of the amine-HONO reaction as a pathway for nitrosamine formation at night is not easily assessed. The low nitrosamine yields (about 1 percent) of Grosjean et al. (1977) and Pitts et al. (1978) were obtained with initial NO and NO₂ levels of 0.08 and 0.16 ppm. Such NO_x levels are typical of most urban atmospheres. There are only limited data for the nitrosamine precursors, HONO and amines. HONO levels at night may reach 8 ppb in Los Angeles (Harris et al., 1982). There are virtually no data on ambient levels of amines. Exhaust from catalyst-equipped cars contains up to 2.2 mg/mile of aliphatic amines, including up to 0.1 mg/mile of dimethylamine (Cadle and Mulawa, 1980). Amine concentrations of 50, 2 and 0.1 ppb, which, in our opinion, may represent extremes and median values in Los Angeles air, would yield 500, 20 and 1 ppt of nitrosamines, respectively.

In the above discussion, in-situ formation of nitrosamine from amines and HONO has been limited to gas phase reactions. Nitrosation of amines in water is well documented in the bulk phase (e.g. Challis and Kyrtopoulos, 1977) and may be relevant to fog and cloudwater. Nitrosamines formation in the human respiratory tract as a result of inhaling air free of nitrosamines but containing amines and HONO may also be considered as an in-situ formation pathway.

13.8.1.2 OH-initiated Photooxidation of Amines

Amines react rapidly with OH ($k \sim 2$ to $10 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$) and the irradiation of amine-NO_x mixtures in air results in the rapid conversion of NO to NO₂ and the formation of ozone, carbonyls, and other products (Grosjean et al., 1977; Pitts et al., 1978; Tuazon et al., 1978). The initial OH attack involves two abstraction pathways, i.e. H atom

abstraction from N-H and H atom abstraction from C-H. The N-H abstraction pathway leads to dialkyl amino radicals, which in turn react slowly with O₂ and rapidly with NO and NO₂ to form nitrosamines and nitramines, respectively:



Lindley et al. (1979) have determined that pathway [1a] = 37 ± 5 percent of the total OH reaction, $k_2/k_3 = 1.5 \times 10^{-6}$, $k_2/k_{4a} = 3.9 \times 10^{-7}$, and $k_{4b}/k_{4a} = 0.22 \pm 0.06$ for dimethylamine. The ratio $k_{1a}/(k_{1a} + k_{1b})$ is not known for diethylamine, but should be lower than for (CH₃)₂NH since (C₂H₅)₂NH contains weaker secondary C-H bonds. Of course, only pathway [1a] is possible for tertiary amines. In this case, dialkylamino radicals form from the alkyl radicals following initial OH attack, as is shown in Figure 13.8-1 for triethylamine. Other reaction products of pathway [1a] include acetamides, aldehydes (and PAN from acetaldehyde), and free radicals.

Reaction mechanisms for triethyl, diethyl, trimethyl, and dimethylamine, consistent with the results of Grosjean et al., Pitts et al., Tuazon et al. and Lindley et al., are outlined in Figures 13.8-1 to 13.8-4. Analogous mechanisms are given in Figure 13.8-5 and 13.8-6 for methylethyl amine and methyldiethylamine, two precursors of methylethyl nitrosamine, which have not been studied experimentally.

13.8.2 Removal Processes

All nitrosamines photolyze rapidly in aqueous solution (e.g. Chow, 1973) and in the gas phase (Bamford, 1939):

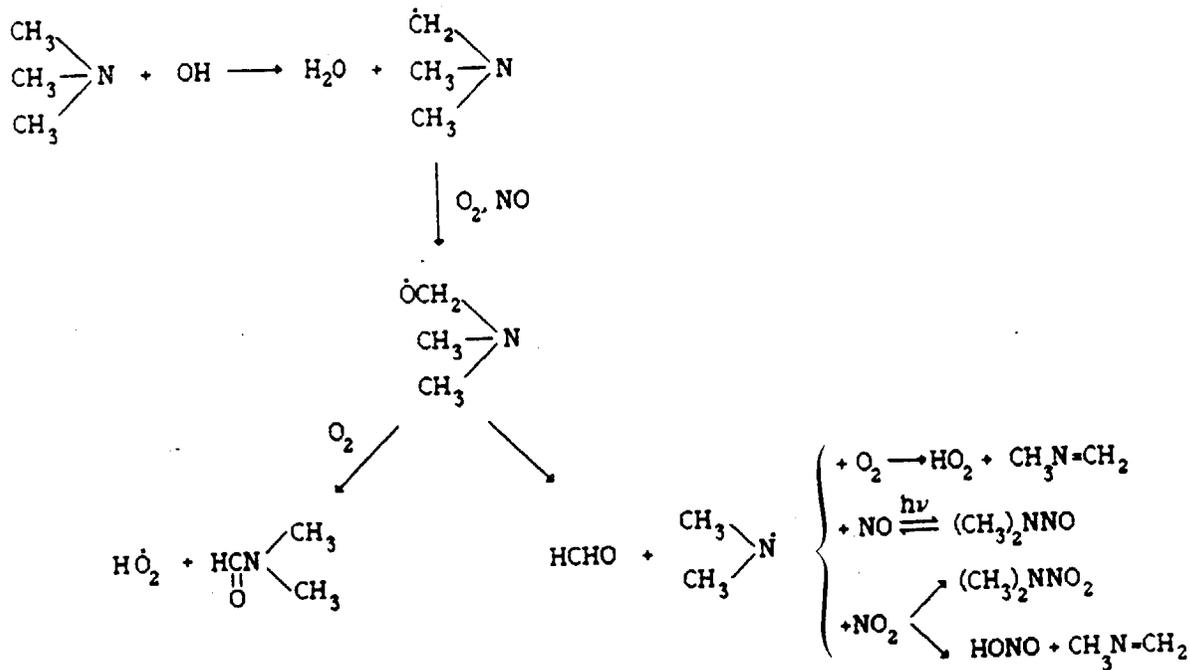


Figure 13.8-3. OH-Trimethylamine Reaction.

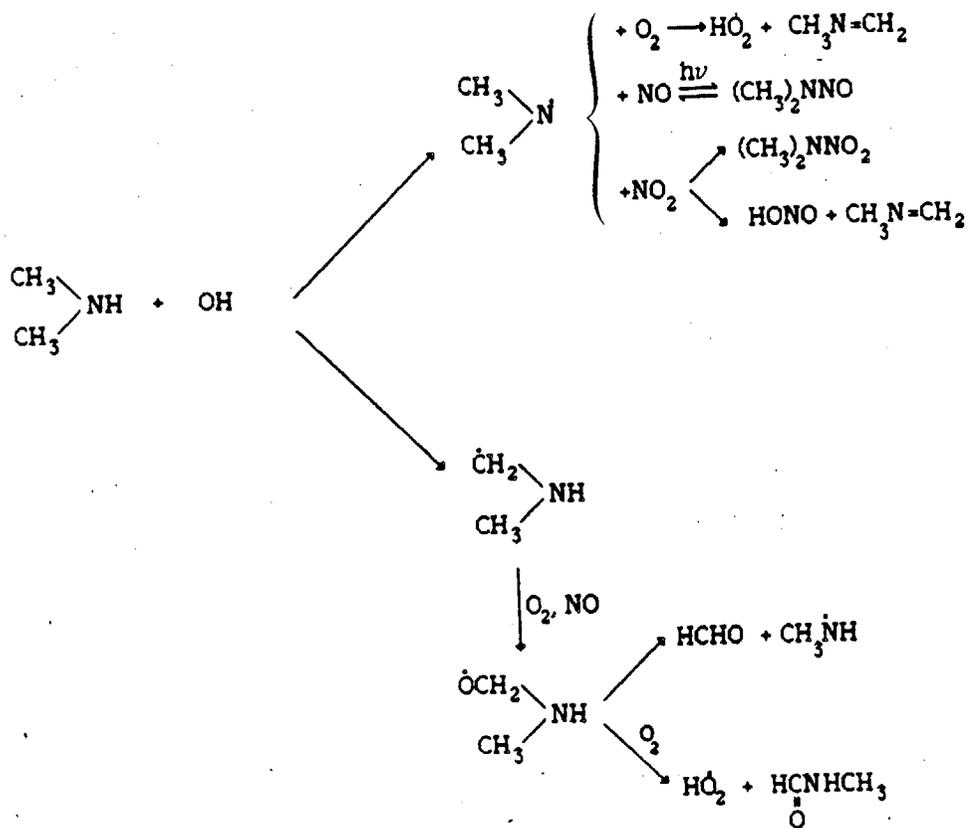
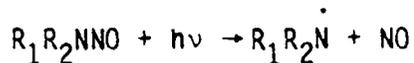


Figure 13.8-4. OH-Dimethylamine Reaction.



In the atmosphere, the dialkyl amino radical thus formed may react with NO, NO₂ and O₂. (See reactions [2], [3], [4a] and [4b] in the preceding section.) Hanst et al. (1977) exposed (CH₃)₂NNO to sunlight in a Teflon reactor and observed photolysis half-lives of 30 minutes in full sunlight and 60 minutes on a cloudy day. Bretschneider and Matz (1976) obtained similar results for (C₂H₅)₂NNO in sunlight. Lindley et al. (1979) obtained a photolysis rate constant of 0.12 ± 0.12 min⁻¹ for (CH₃)₂NNO in sunlight (zenith angle = 40°). This value is assumed to apply to all other nitrosamines, whose photolysis rates have not been measured.

We are then left with the task of estimating nitrosamine levels during daytime, given the competition between their formation by OH + amine reactions and their destruction by photolysis. Experimental results of Pitts et al. (1978) show that diethylnitrosamine formed initially in the dark was destroyed upon exposure of diethylamine - NO_x to sunlight. In this case, nitrosamine loss by photolysis prevailed over nitrosamine formation from the amine-OH reaction. In the case of triethylamine, however, the diethylnitrosamine concentration actually increased for > 60 minutes, at which point loss by photolysis became preponderant. With no available data for ambient levels of amines, let us consider three scenarios corresponding to constant sources of amines resulting in ambient amine levels of 50, 2 and 0.1 ppb. Using typical values of NO = NO₂ = 0.1 ppm and OH = 10⁻⁷ ppm, Lindley et al. (1979) calculate, for a zenith angle of 40°, steady-state dimethylnitrosamine levels of 200, 8 and 0.4 ppt, respectively. By comparison, the data of Gordon (1978) for 15 locations in Los Angeles include averages of 1-31 ppt and maxima of up to 160 ppt. This would suggest amine levels of 1-40 ppb, i.e. somewhat on the high side of the estimated range of concentrations for amines in urban air. These speculations are, of course, no substitute for simultaneous measurements of amines, nitrosamines, NO and NO₂, which have yet to be carried out in ambient air.

Finally, it seems appropriate in this section to mention the other, and major, amine reaction products, namely nitramines (R₂NNO₂) and amides (RCONHR and RCONR₂). The atmospheric fate of amides is unknown. Unlike

nitrosamines, nitramines do not photolyze and are expected to accumulate in the atmosphere (their reactions with OH, O₃, etc. are slow, e.g. k_{OH} + nitramines ≤ k_{OH} + alkanes). Lindley et al. (1979), using the lowest scenario for ambient dimethylamine, 0.1 ppb, estimate that 65 ppt of dimethylnitramine will form after 6 hours in sunlight. Dimethylnitramine (e.g. Goodall and Kennedy, 1976) and acetamide (e.g. Weisburger et al., 1969) are both carcinogens in test animals.

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EVALUATION OF 1,4-DIOXANE

14.1 PHYSICAL AND CHEMICAL PROPERTIES

1,4-dioxane is a volatile, colorless liquid at normal ambient temperatures. Table 14.1-1 summarizes some of its physical and chemical properties.

14.2 DIRECT PRODUCTION IN CALIFORNIA

The four U.S. producers of 1,4-dioxane (CPS Chemical Company, Dow Chemical USA, Ferro Corporation, and Union Carbide Corporation) are all located outside of California (SRI, 1983).

14.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

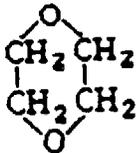
We have identified no industrial processes in California which would lead to the formation of 1,4-dioxane as a byproduct. The only indirect source of this compound would be atmospheric releases during its addition to methyl chloroform as a stabilizer. (See Section 14.4.) However, no methyl chloroform is produced in California (Slimak et al., 1980).

14.4 INDUSTRIAL USE AND EMISSIONS

1,4-dioxane is one of five or six compounds used as stabilizers or reaction inhibitors in methyl chloroform (1,1,1-trichloroethane); its presence inhibits reaction of the methyl chloroform with a variety of metals for which the latter is a degreasing solvent. According to the methyl chloroform manufacturers and distributors contacted for this project, no more than 4 percent by weight of the final product is comprised of 1,4-dioxane; the general range of 1,4-dioxane concentration is about 1 to 3 percent (Dombrowski, 1985; Hughes, 1985).

Reaction inhibition is probably the main industrial use of 1,4-dioxane. It is also used industrially as a solvent for fats, waxes,

Table 14.1-1
 CHEMICAL DATA SUMMARY FOR 1,4-DIOXANE

Property	Value for 1,4-dioxane
CAS Registry No.	123-91-1
Synonyms	p-dioxane; diethylene ether; glycol ethylene ether; 1,4-diethylene dioxide; dioxyethylene ether
Molecular Weight	88.11
Molecular Formula	C ₄ H ₈ O ₂
Molecular Structure	 <p>The diagram shows a six-membered ring structure of 1,4-dioxane. It consists of two oxygen atoms (O) at the top and bottom positions, and four methylene groups (CH₂) at the left and right positions. The atoms are connected by single bonds to form a closed ring.</p>
Physical State at STP	Colorless liquid
Boiling Point	101°C
Melting Point	10°C
Specific Gravity	1.033 @ 20/4°C
Vapor Pressure	30 mm @ 20°C, 37 mm @ 25°C, 50 mm @ 30°C
Vapor Density (air=1)	3.03
Solubility	
Log Partition Coefficient (octanol/H ₂ O)	0.01
Henry's Law Constant	1.07 x 10 ⁻² atm-L/mole

Source: Verschueren (1977), ICF (1985).

greases, paint and varnish strippers, resins, polyvinyl polymers, dyes, and lacquers (NIOSH, 1977). A use which may be particularly relevant to California's film industry is as a solvent for celluloid and similar products where nitrocellulose, cellulose acetate or other cellulose esters or ethers are used. (Whether the 1,4-dioxane used in this industry is used directly or as a methyl chloroform stabilizer is uncertain.)

Table 14.4-1 shows facilities in the South Coast and San Francisco Bay air basins where, according to surveys conducted by the corresponding air quality management districts, 1,4-dioxane is emitted. Examination of the survey forms indicates that most of these emissions occur as a result of the use of 1,1,1-trichloroethane for degreasing, but that some are due to direct use of 1,4-dioxane.

Using information on 1,1,1-trichloroethane shipments through organic chemical bulk terminals in the Los Angeles area, the South Coast Air Quality Management District (SCAQMD) estimated area source emissions of 1,4-dioxane in the South Coast Air Basin (SCAB) (Zwiacher et al., 1983). The SCAQMD assumed that 80 percent of the shipments passing through the Los Angeles area were consumed in the SCAB and that degreasing comprised 70 percent of the methyl chloroform use. Furthermore, the District assumed that 1,4-dioxane was present at 3 percent by volume (about 2.3 percent by weight) in the 1,1,1-trichloroethane used for degreasing and at 1 percent by volume (about 0.8 percent by weight) in the remainder of the 1,1,1-trichloroethane. Zwiacher et al. note that the use of 1,1,1-trichloroethane by the motion picture industry is an example of an application requiring low concentrations of 1,4-dioxane. Total 1,4-dioxane emissions were estimated to be 377 tons in 1982. Note that it was assumed that 100 percent of the methyl chloroform (and 1,4-dioxane) used in the SCAB was also emitted.

The same approach can be used on a statewide basis by using methyl chloroform material balance data obtained by SAIC in a previous study for the ARB (Rogozen et al., 1985). Since the material balance took into account recycling of methyl chloroform and some degree of pollution control, the results are not exactly comparable. The SAIC study estimated that 12,765 ± 1,453 tons/yr of 1,1,1-trichloroethane were emitted in 1980 in California as

Table 14.4-1
1,4-DIOXANE EMISSIONS REPORTED BY THE BAY AREA AND SOUTH
COAST AIR QUALITY MANAGEMENT DISTRICTS

Firm	City	County	SCAQMD		BAAQMD	
			lb/yr	kg/yr	lb/yr	kg/yr
A-H Plating Inc.	Burbank	Los Angeles	76	34.5	-	-
Acto Kleen Company	Pico Rivera	Los Angeles	1	0.5	-	-
Airesearch Div., Garrett Corp.	Torrance	Los Angeles	1	0.5	-	-
American Bentley	Irvine	Orange	4	1.8	-	-
Beckman Instruments, Inc.	Palo Alto	Santa Clara	-	-	T ^a	T
California & Hawaiian Sugar	Crockett	Contra Costa	-	-	T	T
Calusa Chemical Company, Inc.	Santa Fe Springs	Los Angeles	1	0.5	-	-
Chevron Research Company	Richmond	Contra Costa	-	-	400	180
Clorox Technical Center	Pleasanton	Alameda	-	-	U ^a	U
DOE-Sandia National Laboratory	Livermore	Alameda	-	-	T	T
Dysan Corporation	Santa Clara	Santa Clara	-	-	T	T
Genentech, Inc.	S. San Francisco	San Mateo	-	-	T	T
Hi-Shear Corporation	Torrance	Los Angeles	34	15.4	-	-
IT Corporation, Oil Reprocessing	Martinez	Contra Costa	-	-	U	U
IT Corporation, Vine Hill	Martinez	Contra Costa	-	-	T	T
Koppers Company, Inc.	Richmond	Contra Costa	-	-	T	T
Lawrence Livermore National Lab.	Livermore	Alameda	-	-	T	T
Lockheed Missiles & Space Division	Sunnyvale	Santa Clara	-	-	T	T
MGM Studios	Culver City	Los Angeles	1	0.5	-	-
Micro-Biothrol Company	Vernon	Los Angeles	1	0.5	-	-
Narmco Materials Inc.	Anaheim	Orange	1	0.5	-	-
National Semiconductor Corporation	Santa Clara	Santa Clara	-	-	T	T
Naval Air Station Alameda	Alameda	Alameda	-	-	U	U
Prescolite, Div. of U.S.I.	San Leandro	Alameda	-	-	T	T
Raychem Corporation	Menlo Park	San Mateo	-	-	U	U
Robertshaw Controls Company	Long Beach	Los Angeles	5,252	2,381.9	-	-
Rohr Industry Inc.	Riverside	Riverside	1,205	546.5	-	-
Shell Oil Company	Martinez	Contra Costa	-	-	T	T
SRI International	Menlo Park	San Mateo	-	-	T	T
Stanford Linear Accelerator	Menlo Park	San Mateo	-	-	T	T
Syntex (USA), Inc.	Palo Alto	Santa Clara	-	-	T	T
Towne Paulsen & Company, Inc.	Monrovia	Los Angeles	1	0.5	-	-
Union Oil of Cal, S/T Division	Brea	Orange	1	0.5	-	-
University of California	Berkeley	Alameda	-	-	T	T
Totals			6,579	2,983.7	400	180

Source: Summarized from emissions reported by the South Coast Air Quality Management District (Zwiacher et al., 1983) and the Bay Area Quality Management District (Hill, 1985).

^aT = Emissions are 0-0.1 ton/yr; U = 1,4-dioxane is used but emissions are unknown.

a result of direct industrial use other than incorporation in formulations. The breakdown between degreasing and non-degreasing solvent applications was not determined. Assuming the same breakdown used by the SCAQMD results in a weighted average 1,4-dioxane content of 1.85 percent dioxane by weight. Statewide emissions, using the SAIC data, would therefore be 209 to 263 tons/yr. This number is lower than the SCAQMD estimate for the SCAB alone because (1) it is based upon emissions rather than use and (2) the 1,4-dioxane content assumed for the SCAB may not be appropriate for other parts of the state. Indeed, if an average of 3 percent 1,4-dioxane by weight is assumed, then the SAIC statewide estimate would be 339 - 427 tons. In any event, emissions of 1,4-dioxane are probably less than 1000 tons per year in California.

14.5 CONSUMER USE AND EMISSIONS

Very little information has been obtained on the use of 1,4-dioxane in consumer products or on consumer exposure. The compound is present in some paint and varnish strippers (Sittig, 1981), and would likely be included in some of the methyl chloroform used in consumer formulations. The aforementioned SAIC study for the ARB estimated that about 80 tons of methyl chloroform were emitted in 1980 through the use of consumer products such as spot removers. If the lower end of the the SCAQMD's estimate of 1,4-dioxane content (1 percent by volume) is used, then emissions from consumer products would be less than 1 ton per year.

14.6 EMISSION SUMMARY

No 1,4-dioxane is produced, used as a feedstock, or released as a byproduct of any manufacturing process in California. The main use of the compound is as a reaction inhibitor in methyl chloroform (1,1,1-trichloroethane). Although there is some discrepancy between different estimates of methyl chloroform use in the state, corresponding 1,4-dioxane emissions are probably between about 200 and 600 tons per year.

14.7 SUMMARY OF AMBIENT CONCENTRATION DATA

No data are available for ambient concentrations of 1,4-dioxane in California or elsewhere.

14.8 ATMOSPHERIC CHEMISTRY

14.8.1 In-Situ Formation

There is no known reaction that would lead to the in-situ production of dioxane in the atmosphere.

14.8.2 Removal Processes

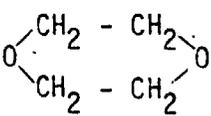
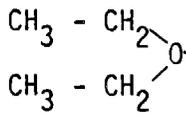
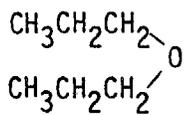
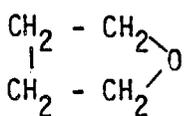
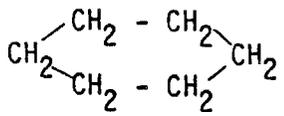
No data are available concerning kinetic and product studies of dioxane reactions relevant to its atmospheric persistence. Loss by photolysis, by reaction with ozone and by reaction with the nitrate radical are negligible.

Reaction of dioxane with the hydroxyl radical is sufficiently rapid to represent a substantial loss process during daytime. The OH-dioxane reaction rate constant we estimate from structure-reactivity relationships (see Chapter 3) is about $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. This estimate compares well with those measured for other ethers of similar structure (Table 14.8-1) and also for cyclohexane, considering that C-H bond energies in ethers are slightly lower than those in alkanes (93 vs. 95 kcal/mole), thus resulting in slightly higher rates of H-atom abstraction by OH.

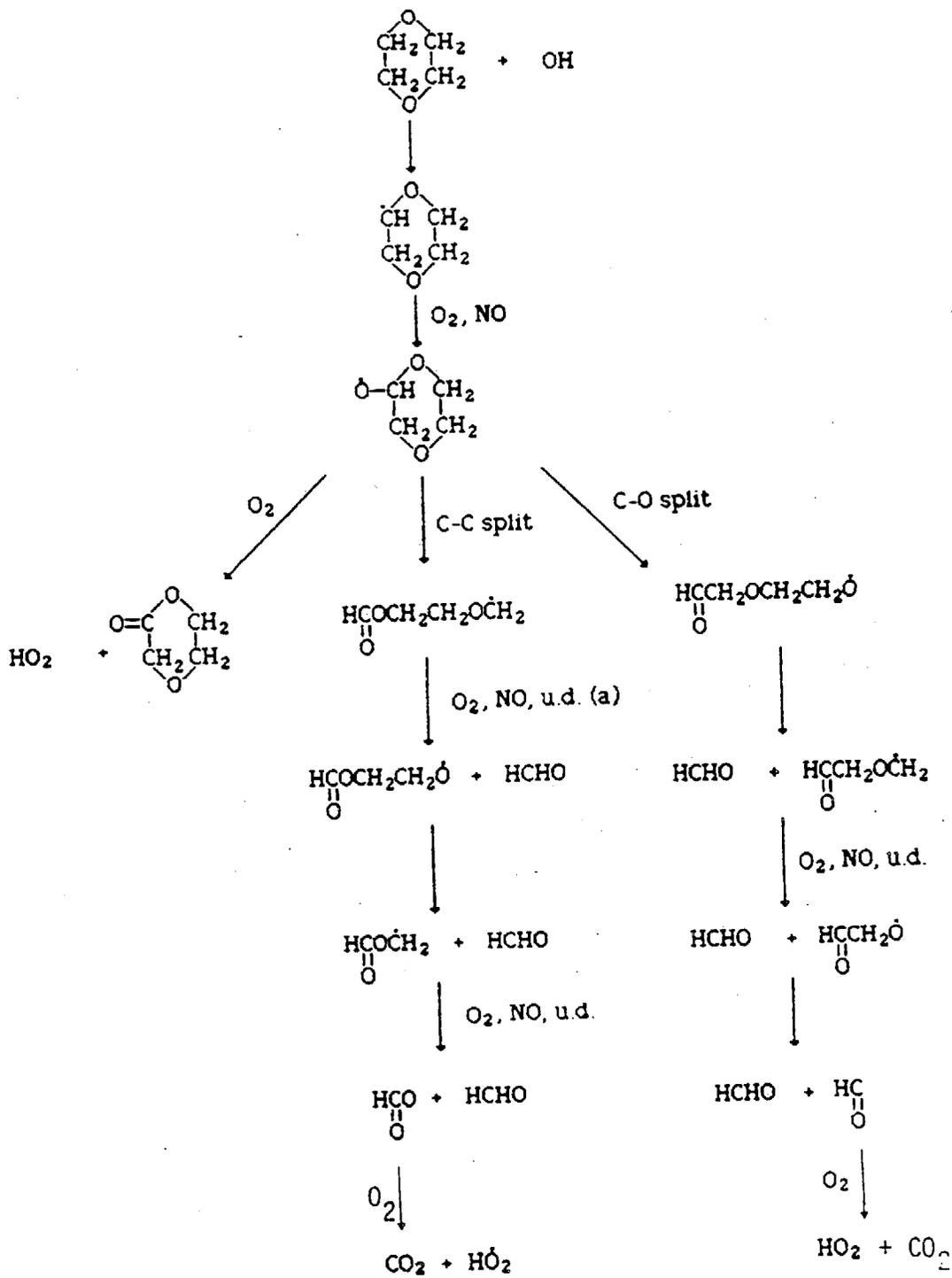
A tentative mechanism for the OH-dioxane reaction is given in Figure 14.8-1. All hydrogen atoms being equivalent, only one alkyl radical is formed in the initial reaction step. The corresponding alkoxy radical may undergo unimolecular decomposition or react with O_2 to form 2-oxo dioxane. The relative importance of the two pathways is unknown. Unimolecular decomposition may involve scission of either C-C or C-O bonds (81-83 vs 85 kcal/mole), and both pathways are shown in Figure 14.8-1. Each pathway leads to three molecules of formaldehyde plus CO or CO_2 .

Table 14.8-1

OH REACTION RATE CONSTANTS OF SELECTED
ETHERS AND STRUCTURAL ANALOGUES OF DIOXANE

Compound	Structure	k_{OH} , $\text{cm}^{-3} \text{ molecule}^{-1} \text{ sec}^{-1}$	Comments
Dioxane		2×10^{-11}	Estimated from structure-reactivity relationship ^a
		1.4×10^{-11}	Estimated from Greiner's formula ^b for ethers
Diethylether		0.89×10^{-11}	Only 4 secondary H atoms vs 8 in dioxane
Di-n-propylether		1.63×10^{-11}	8 secondary H atoms, same as in dioxane
Tetrahydrofuran		1.60×10^{-11}	8 secondary H atoms, same as in dioxane
Cyclohexane		0.8×10^{-11}	Replace O atoms in dioxane by CH_2 groups, increase C-H bond energies by 2 kcal/mole each.

^a See Chapter 3.^b $k_{OH} = 6 \times 10^{-13} \times (\text{number of primary H}) + 1.7 \times 10^{-12} \times (\text{number of secondary H})$.



(a) u.d. = unimolecular decomposition

Figure 14.8-1 OH-Dioxane Reaction.

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EVALUATION OF EPICHLOROHYDRIN

15.1 PHYSICAL AND CHEMICAL PROPERTIES

Epichlorohydrin is a colorless liquid. Table 15.1-1 summarizes some of its physical and chemical properties.

15.2 DIRECT PRODUCTION IN CALIFORNIA

Epichlorohydrin is produced by two companies, Dow Chemical Company and Shell Chemical Company, at three locations outside California (Peterson, 1980). There is no California production.

15.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

As mentioned in Section 15.8, some epichlorohydrin may form through atmospheric reaction; the amount is likely to be quite small. We are unaware of other means of indirect production of this compound.

15.4 INDUSTRIAL USE AND EMISSIONS

Epichlorohydrin is used extensively as a chemical intermediate in the production of a variety of chemical compounds. Crude epichlorohydrin is used to produce synthetic glycerin, while finished epichlorohydrin is used principally in the production of epoxy resins (Thomas, 1985). In 1978, the last year for which consumption pattern data were available, epoxy resin manufacture consumed 56 percent of the compound's production, and conversion to synthetic glycerin consumed another 25 percent (Peterson, 1980). Two percent of production was directed toward the manufacture of elastomers, which were in turn used to produce epichlorohydrin rubber for automobile parts, seals and gaskets, wire cable jackets, hose and belting, adhesives, and rubber coating fabrics. Approximately 12 percent of epichlorohydrin production went into miscellaneous other products such as polyamide epichlorohydrin resins; water treatment resins; flame retardants; solvents for various resins, gums, cellulose esters and ethers, paints, varnishes, lacquers, and nail enamels;

Table 15.1-1
CHEMICAL DATA SUMMARY FOR EPICHLOROHYDRIN

Property	Value for Epichlorohydrin
CAS Registry No.	106-89-8
Synonyms	3-chloro-1, 2-propylene, 3-chloro-1-oxacyclobutane, 3-chlorooxetane, chloromethyl- oxirane, dl- α -epichlorohydrin, 1-chloro-2, 3-epoxypropane, γ -chloropropylene oxide, ECH
Molecular Weight	92.53
Molecular Formula	C_3H_5ClO
Molecular Structure	$\begin{array}{c} O \\ \diagup \quad \diagdown \\ CH_2 - CH - CH_2Cl \end{array}$
Physical State at STP	Colorless liquid
Boiling Point	117.9 $^{\circ}C$
Melting Point	-25.6 $^{\circ}C$
Specific Gravity	1.1801 at 20 $^{\circ}C/4^{\circ}C$
Vapor Pressure	16.8 mm at 25 $^{\circ}C$
Vapor Density (air=1)	3.19
Solubility	Insoluble (H ₂ O)
Log Partition Coefficient (octanol/H ₂ O)	0.15
Henry's Law Constant	0.0319 atm-L/mole

Source: SAI (1980), ICF (1985).

heat stabilizers for plastics; a sporicide; dyestuffs; pharmaceuticals; and lubricants (Santodonato et al., 1980; SRI, 1981). The compound is also added as a stabilizer for chlorinated rubber and insecticides and as an inactive ingredient in several pesticides (Santodonato et al., 1980). In 1978, five percent of production was exported. Estimated 1982 production was 170,000 metric tons, with a projected annual growth rate of 5.4 percent.

Because epoxy resin manufacturing accounts for such a high percentage of epichlorohydrin use, SAIC attempted to identify all such manufacturers in the State. The 1983 Directory of Chemical Producers (SRI, 1983) lists 13 epoxy resin producers in California. SAIC contacted six of these producers to ascertain whether they used epichlorohydrin as an intermediate or were aware of other firms which did. All firms indicated that they did not directly handle epichlorohydrin. The general attitude expressed was that the compound was "too toxic" and heavily regulated to be worth the trouble, especially when other materials were available (Baven, 1985; Cox, 1985; Edwards, 1985; Keefer, 1985; Miyada, 1985; Sitze, 1985). We are therefore fairly confident that no epichlorohydrin is used in California for epoxy resin formulation.

All epichlorohydrin used in the manufacture of synthetic glycerin is produced at the same two plants in Texas that manufacture the glycerin (Santodonato et al., 1980). Epichlorohydrin elastomers are produced at two locations, in Ohio and Mississippi. When exports are accounted for, use of 88 percent of the annual production of epichlorohydrin occurs outside California. How the remaining 12 percent is apportioned among the states is unknown. However, estimates of epichlorohydrin emissions in the San Francisco Bay Area and the South Coast Air Basin are available from the respective air quality management districts (Hill, 1985; Zwiacher et al., 1983). According to surveys conducted by these districts, 30 firms use at least small quantities of epichlorohydrin. (See Table 15.4-1.) Emissions in the two districts total 134 lb/year (61 kg/yr). In its calculations, the South Coast Air Quality Management District assumed an uncontrolled emission factor of 0.01 lb per lb of epichlorohydrin used. A nominal 1 lb/yr emission rate was assigned to facilities having closed systems and/or controls. For none of the facilities which the Bay Area Air Quality Management District reported as epichlorohydrin

Table 15.4-1

EPICHLOROHYDRIN EMISSIONS REPORTED BY THE BAY AREA
, AND SOUTH COAST AIR QUALITY MANAGEMENT DISTRICTS

Firm	City	County	SCAQMD		BAAQMD	
			lb/yr	kg/yr	lb/yr	kg/yr
Ace Rubber Company	South Gate	Los Angeles	1	0.5	-	-
Acto Kleen Company	Pico Rivera	Los Angeles	1	0.5	-	-
Alameda Naval Air Station	Alameda	Alameda	-	-	U ^a	U
Amplex Corporation	Alameda	San Mateo	-	-	U	U
Burke Industries, Inc.	San Jose	Santa Clara	-	-	-	-
Cooke Lab. Products Corp.	Commerce	Los Angeles	6	2.7	-	-
Custom Rubber Mix, Inc.	Los Angeles	Los Angeles	2	0.9	-	-
Dow Chemical Company	Pittsburg	Contra Costa	-	-	-	-
Dunn-Edwards Corp.	Los Angeles	Los Angeles	1	0.5	-	-
Dysan Corporation	Santa Clara	Santa Clara	-	-	-	-
Fairchild Camera and Instr.	San Jose	Santa Clara	-	-	-	-
Ford Aerospace and Communications	Palo Alto	Santa Clara	-	-	-	-
Fuller-O'Brien	S. San Francisco	San Mateo	-	-	-	-
Global Processing Corp.	Santa Fe Springs	Los Angeles	1	0.5	-	-
Gould Inc.	El Monte	Los Angeles	10	4.5	-	-
Hewlett-Packard Company	Santa Rosa	Sonoma	-	-	-	-
Hewlett-Packard Company	Sunnyvale	Santa Clara	-	-	-	-
Koppers Company, Inc.	Vernon	Los Angeles	3	1.4	-	-
Lawrence Livermore Nat. Lab.	Livermore	Alameda	-	-	-	-
Magna Corp.	Santa Fe Springs	Los Angeles	54	24.5	-	-
Master Processing Corp.	Long Beach	Los Angeles	1	0.5	-	-
Nalco Chemical Company	Carson	Los Angeles	1	0.5	-	-
Plaskon Products Inc.	Los Angeles	Los Angeles	1	0.5	-	-
Rohr Ind. Inc.	Riverside	Riverside	20	9.1	-	-
Sherwin-Williams Company	Emeryville	Alameda	-	-	-	-
Tretolite, Div. Petrolite Corp.	Brea	Orange	32	14.5	-	-
U.S. Pipe and Foundry	Union City	Alameda	-	-	-	-
United Technologies	San Jose	Santa Clara	-	-	-	-
Van Waters and Rogers	San Jose	Santa Clara	-	-	-	-
Xidex Corporation	Sunnyvale	Santa Clara	-	-	-	-
Total			134	60.8	0	0

Source: Data summarized from Hill (1985) and Zwiacher et al. (1983).

^aT = 0 to 0.1 tons/yr; U = epichlorohydrin is handled but emissions cannot be estimated from available information.

users or handlers could emissions be estimated, although the District believes that they do not exceed 0.1 ton/year in any case.

15.5 CONSUMER USE AND EMISSIONS

As discussed in Section 15.4, most epichlorohydrin is used as an intermediate in the manufacture of various chemicals; very little is sold on the open market. Possible consumer uses having a potential for volatilization of epichlorohydrin include: solvent use in paints, varnishes, lacquers, and nail enamels; and sporicide use. The consumer products, mentioned in Section 15.4, that are made from epichlorohydrin elastomers may contain some epichlorohydrin as a trace contaminant. It is not possible at this time to quantify the production of such consumer goods, their California distribution, or the emissions which could result from their California use .

15.6 EMISSION SUMMARY

Epichlorohydrin is not produced deliberately in California, although small amounts of the compound may be generated in the atmosphere. Epichlorohydrin is used primarily to manufacture epoxy resins and synthetic glycerin; all facilities for such production are located outside California. Less than 0.1 ton/year of epichlorohydrin emissions occur from various other manufacturing uses in the San Francisco Bay and South Coast air basins. Consumer products which contain epichlorohydrin include paints, varnishes, lacquers, nail enamels, and pesticides. Small amounts of the chemical may be trapped as a contaminant in epichlorohydrin elastomer products. It appears that the use of products which contain epichlorohydrin might be widespread; however, it is not presently possible to quantify the distribution of such products or their epichlorohydrin emissions.

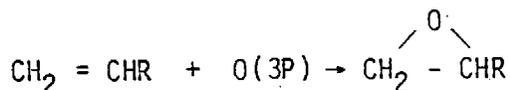
15.7 SUMMARY OF AMBIENT CONCENTRATION DATA

There are no data available for ambient or near-source levels of epichlorohydrin.

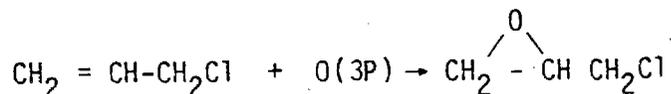
15.8 ATMOSPHERIC CHEMISTRY

15.8.1 In-Situ Formation

The reaction of atomic oxygen with olefins leads to epoxides:



Accordingly, epichlorohydrin may form by reaction of atomic oxygen with 3-chloropropene (allyl chloride)



This reaction is not, however, expected to be of importance in ambient air. Allyl chloride also rapidly reacts with OH and with ozone as discussed in detail in Section 7.8.2. Concentrations of O(3P) in the atmosphere relative to those of OH and O₃ are too low for the allyl chloride-O(3P) reaction to compete with the allyl chloride-OH and allyl chloride-O₃ reactions.

15.8.2 Removal Processes

There have been no kinetic or product studies relevant to the atmospheric removal of epichlorohydrin. Photolysis, reaction with O₃ and reaction with NO₃ are negligible. Slow removal by reaction of epichlorohydrin with OH is expected. The rate constant for the OH-epichlorohydrin reaction, estimated from structure-reactivity relationships, is about $3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. This estimated rate constant compares well with those measured for structural analogues, including other epoxides such as epoxypropane and 1,2-epoxybutane ($k_{\text{OH}} = 1.3 \times 10^{-12}$ and $2.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, respectively).

A tentative scheme for the slow removal of epichlorohydrin by OH-initiated photooxidation in the atmosphere is outlined in Figure 15.8-1. This mechanism is identical to that proposed in Chapter 26 for the OH-

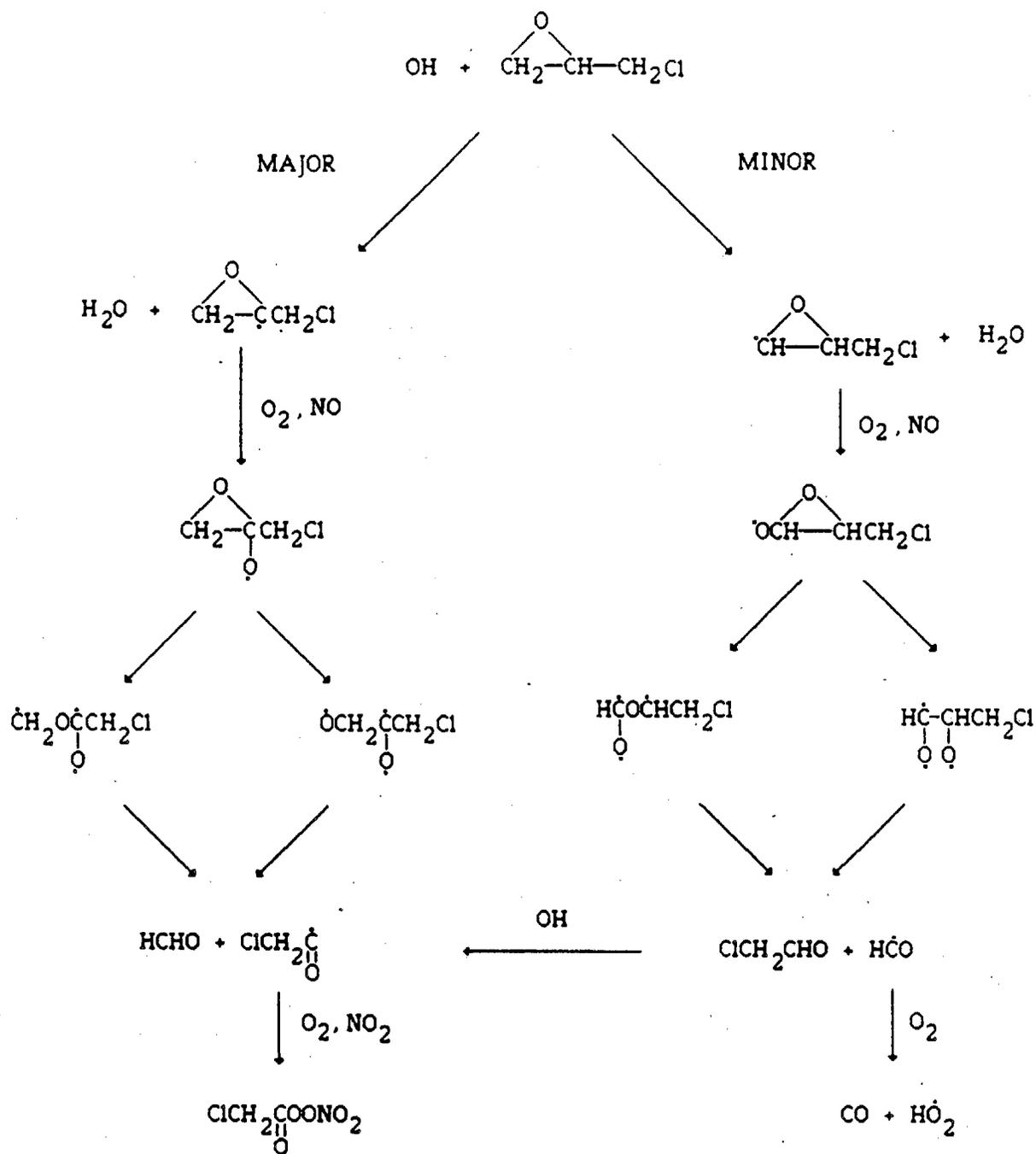


Figure 15.8-1. OH-Epichlorohydrin Reaction.

propylene oxide reaction. H-atom abstraction is expected to involve the tertiary C₂ hydrogen atom and, to a lesser extent, the secondary C₁ hydrogen atoms. Both pathways are included in Figure 15.8-1. For both alkoxy radicals, unimolecular decomposition may involve C-C as well as C-O bond scission, leading to formaldehyde, ClCH₂CO, chloroacetaldehyde, and HCO. The major product expected to form from both chloroacetaldehyde (by reaction with OH) and the chloroacetyl radical ClCH₂CO is ClCH₂COONO₂, monochloro

peroxyacetylnitrate. This compound, along with other substituted PANs, has been identified in laboratory experiments involving the appropriate precursors, e.g. chloroacetaldehyde or chlorinated olefins. It has never been identified in ambient air.

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16.0
EVALUATION OF GLYCOL ETHERS

16.1 PHYSICAL AND CHEMICAL PROPERTIES

Although at least six glycol ethers are used commercially in California (Rogozen et al., 1983), this evaluation has focused upon the three which previous research has shown to be the most commonly used in the state: ethylene glycol monomethyl ether (EGMME), ethylene glycol monoethyl ether (EGMEE), and ethylene glycol monobutyl ether (EGMBE). All are colorless liquids at standard temperature and pressure. Tables 16.1-1 through 16.1-3 summarize their physical and chemical properties.

16.2 DIRECT PRODUCTION IN CALIFORNIA

Glycol ethers are derived from propylene oxide and ethylene oxide. The ethylene oxide process produces over 90 percent of glycol ethers in the U.S. In 1980 glycol ethers derived from ethylene oxide were produced by seven companies at ten locations, none of which was in California. Three companies (the Dow Chemical Company, Olin Corporation, and Union Carbide Corporation) produced propylene oxide-derived glycol ethers. None of this production occurred in California either (Schomer, 1980)

The current nationwide trend is for a reduction in the use of ethylene glycol ethers. After December 31, 1985, Shell Chemical Company planned to cease marketing ethylene glycol monoethyl ether. After that date, the only EGMEE producers in the U.S. will be Eastman Chemical and Union Carbide (Anon., 1985).

16.3 INDIRECT PRODUCTION IN CALIFORNIA

As discussed in Section 16.8, there are no known reactions leading to the in-situ formation of glycol ethers in the atmosphere. We are not aware of other indirect pathways to the production of these compounds.

Table 16.1-1
 CHEMICAL DATA SUMMARY FOR ETHYLENE GLYCOL MONOMETHYL ETHER

Property	Value for Ethylene Glycol Monomethyl Ether
CAS Registry No.	
Synonyms	ethoxol, ethylglycol, cellosolve, glycolmonethylether, 2-methoxy-ethanol, "Dowanol EE," Oxitol
Molecular Weight	90.1
Molecular Formula	$C_4H_{10}O_2$
Molecular Structure	$HOCH_2CH_2OCH_3$
Physical State at STP	Colorless liquid
Boiling Point	135.1°C
Melting Point	(pour point) -100°C
Specific Gravity	0.9360 g/ml at 50°C/15°C
Vapor Pressure	3.8 mm Hg at 20°C
Vapor Density (air=1)	3.10
Solubility	(Water solubility) Infinite
Log Partition Coefficient (octanol/H ₂ O)	
Henry's Law Constant	

Source: SAI (1980); Verschueren (1977).

Table 16.1-2
 CHEMICAL DATA SUMMARY FOR ETHYLENE GLYCOL MONOETHYL ETHER

Property	Value for Ethylene Glycol Monoethyl Ether
CAS Registry No.	110-80-5
Synonyms	ethoxol; ethylglycol; cellosolve; glycolmonoethylether; 2-ethoxyethanol; "Dowanol EE; Oxitol"
Molecular Weight	90.1
Molecular Formula	$C_4H_{10}O_2$
Molecular Structure	$HOCH_2CH_2OCH_2CH_3$
Physical State at STP	Colorless liquid
Boiling Point	135.1°C
Melting Point	(pour point) -100°C
Specific Gravity	0.9360 g/ml at 50°C/15°C
Vapor Pressure	3.8 mm Hg at 20°C
Vapor Density (air=1)	3.10
Solubility	(Water solubility) Infinite
Log Partition Coefficient (octanol/H ₂ O)	
Henry's Law Constant	

Source: SAI (1980), Verschueren (1977).

Table 16.1-3

CHEMICAL DATA SUMMARY FOR ETHYLENE GLYCOL MONOBUTYL ETHER

Property	Value for Ethylene Glycol Monobutyl Ether
CAS Registry No.	111-76-2
Synonyms	2-butoxyethanol
Molecular Weight	118.2
Molecular Formula	$C_6H_{14}O_2$
Molecular Structure	$HOCH_2CH_2O(CH_2)_3CH_3$
Physical State at STP	Liquid
Boiling Point	171.2 ^o C
Melting Point	(pour point) -75 ^o C
Specific Gravity	0.9027 g/ml at 20 ^o C/4 ^o C
Vapor Pressure	0.76 mm Hg at 20 ^o C
Vapor Density (air=1)	4.08
Solubility	(Water solubility) Infinite
Log Partition Coefficient (octanol/H ₂ O)	
Henry's Law Constant	

Source: SAI (1980).

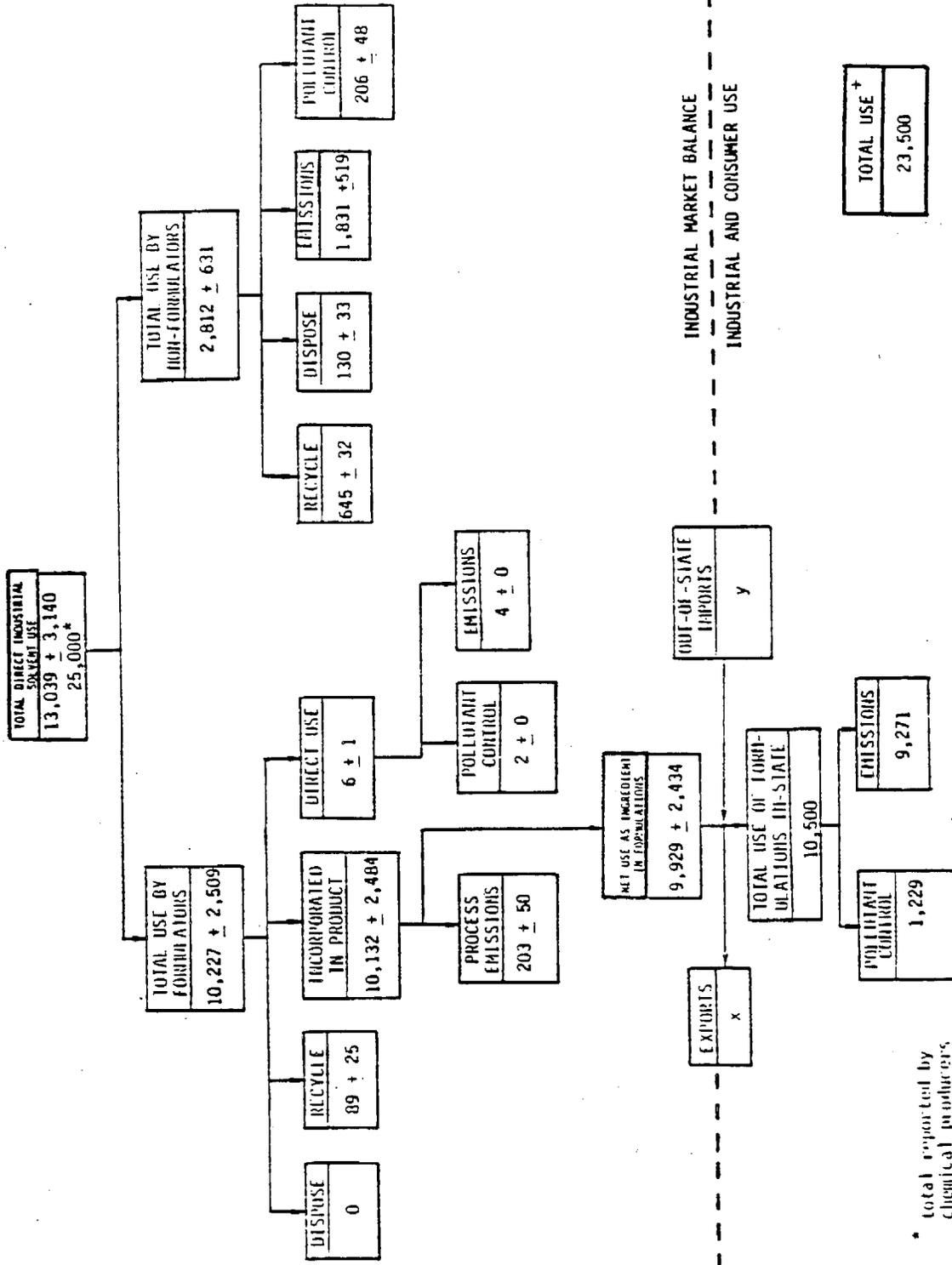
16.4 INDUSTRIAL USE AND EMISSIONS

EGMME is used as a jet fuel additive and solvent in protective coatings such as lacquers, metal coatings, baking enamels, phenolic varnishes, epoxy resin coatings, and alkyd resins, as well as in nitrocellulose and printing inks. It is also an additive to textile and leather dyes and pigments (USDHHS, 1983). EGME is used primarily to produce ethylene glycol monoethyl ether acetate and also as a solvent for protective coatings; a smaller portion of production is used as a solvent for printing inks, and for miscellaneous other purposes. EGMBE is a solvent for protective coatings, metal cleaners, and liquid household cleaners; and is a diluent in hydraulic brake fluids, rust removers, insecticides, and herbicides. It has also been used in the synthesis of 2-butoxyethyl acetate and di (2-butoxyethyl) phthalate (Schomer, 1980; SRI, 1972).

16.4.1 SAIC Survey

SAIC conducted a detailed market balance of EGME and EGMBE in California, based upon 1980 data (Rogozen et al., 1985). Figures 16.4-1 and 16.4-2 summarize the flow of these compounds through the state. Data on direct industrial use were obtained by a written survey of manufacturing firms and chemical and coating formulators.

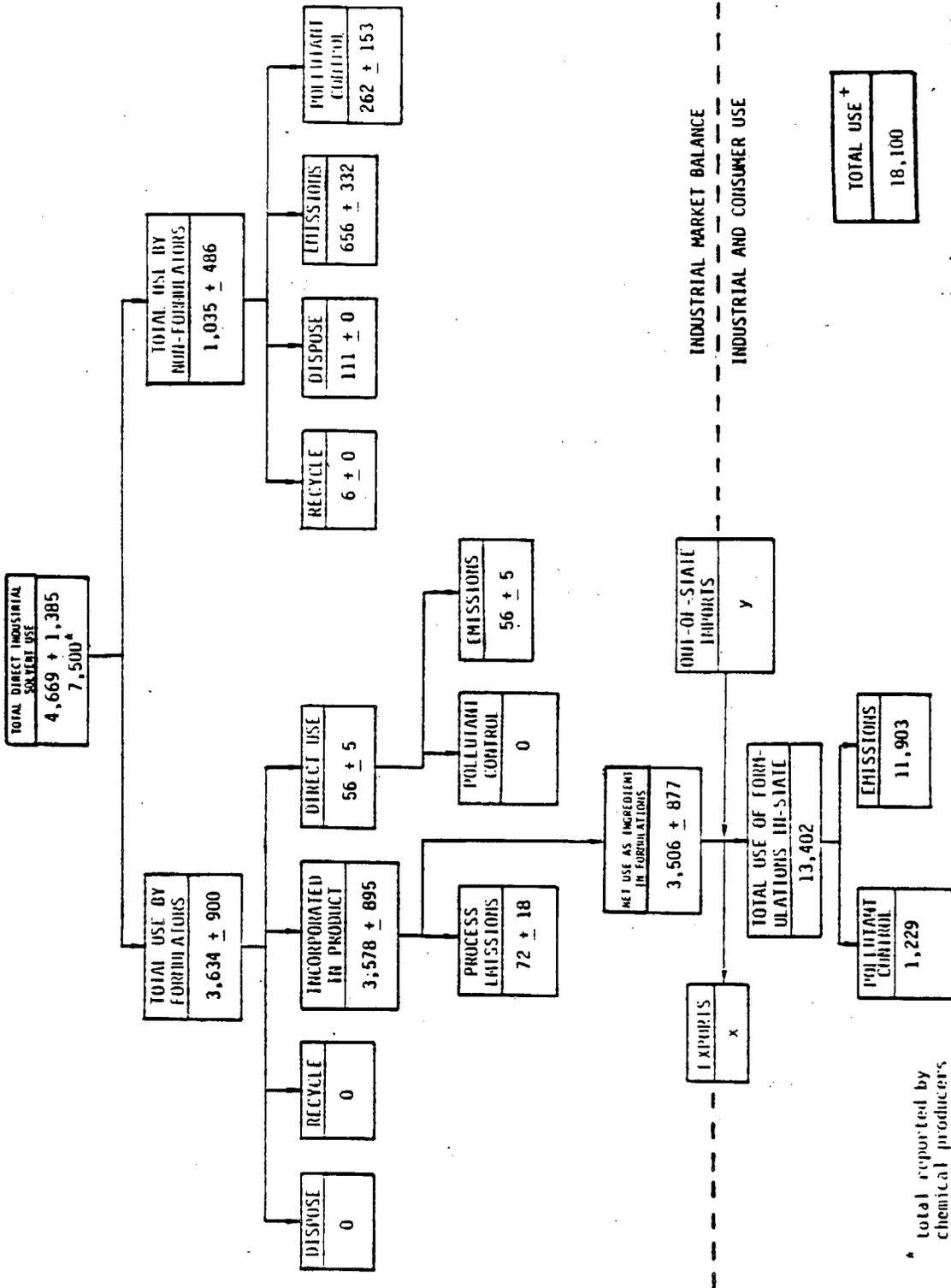
Total direct industrial use of EGMBE was over 13,000,000 lb (6,500 tons), while that of EGME was over 4,700,000 lb (2,300 tons) (Rogozen et al., 1985). Nearly 58 percent and 44 percent, respectively, was accounted for by companies in SIC code 2851 (paints, varnishes and allied products manufacturers). Despite the large fractions of these two compounds accounted for by paints and varnishes, two factors militate against the importance of SIC code 2851 in glycol ether emissions. The first is that, at present, a "major reformulation" effort is under way in the coatings industry to minimize or eliminate ethylene glycol monoethyl ether and ethylene glycol monomethyl ethers (Trehitt and Bluestone, 1985). The second is that the proportion of emissions by formulators, such as those in SIC code 2851, which handle most of the direct use for the glycol ethers (Figures 16.4-1 and 16.4-2), is very small; for example, the fraction of total direct use emissions by EGMBE



* total reported by chemical producers

+ Total use = direct industrial solvent use + total use of formulations in-state

Figure 16.4-1. Market Balance Summary for Ethylene Glycol Monobutyl Ether, 1980 (in 1000 lb) (Rogozen et al., 1985).



* total reported by chemical producers

† Total use = direct industrial solvent use + total use of formulations in-state

Figure 16.4-2. Market Balance Summary for Ethylene Glycol Monoethyl Ether, 1980 (in 1000 lb) (Rogozen et al., 1985).

formulators is 0.002, while for EGME the fraction is 0.08.

Formulators, companies which manufacture products containing EGMBE, consumed over 10,000,000 lb (5,000 tons) and emitted 4,000 lb (2 tons) of the compound to the atmosphere, while all other industrial companies used approximately 2,800,000 lb (1,400 tons) of the compound and emitted over 1,800,000 lb (900 tons). Emissions of EGMBE from products containing EGMBE by both industrial and consumer users was over 9,000,000 lb (4,500 tons) (Figure 16.4-1). We estimated emissions of glycol ethers for both industrial and consumer uses from National Paint and Coatings Association (NPCA) data (Table 16.4-1). The ratio of industrial to consumer use of glycol ethers in California is 0.90 (24.9/27.7). Using this ratio in conjunction with emissions of EGMBE by both industrial and consumer users, we calculate emissions of 4,050 tons/yr due solely to industrial uses. Thus, total emissions of EGMBE in California in 1980 were estimated to be 4,950 tons.

Formulators consumed approximately 3,600,000 lb (1,800 tons) of EGME and emitted 56,000 lb (26 tons) (Figure 16.4-2), while non-formulators emitted approximately 650,000 lb (325 tons). Industrial and consumer users of products containing EGME emitted approximately 12,000,000 lb (6,000 tons). Using the NPCA industrial to consumer ratio of glycol ether use of 0.90, we calculated emissions from industrial use to be 5,400 tons. Thus, total emissions of EGME in 1980 were estimated to be 5,750 tons.

Although a complete market balance was not performed on EGME, the compound was included in the survey of direct industrial users of glycol ethers. Total direct industrial use of EGME in California is 3,300,000 lb (1,650 tons). Although we do not have data on emissions, it is reasonable to assume that the proportion of this glycol ether emitted to the atmosphere is similar to those of the other two glycol ethers for which data exist. The fractions of EGME and EGMBE emitted are 0.15 and 0.14, respectively (712/4669 and 1,837/13,739; see Figures 16.4-1 and 16.4-2). Thus, we estimate that (0.15)(3,300,000 lb), or 495,000 lb (248 tons) EGME are directly emitted by industrial users. Sufficient data do not exist to estimate industrial and consumer emissions of EGME from use of formulated products.

Table 16.4-1
GLYCOL ETHER USE IN PAINTS AND COATINGS

Category	Product	Basis of Apportionment ^a	Apportionment Value		CA/U.S. Ratio	Glycol Ether Use (million lb/yr)	
			U.S.	CA		U.S. ^b	CA
1	Wood Furn. & Fixt.	MPWH	391.5	45.6	0.116	5.00	0.58
2	Wood Flat Stock	MPWH	94.0	6.7	0.071	3.00	0.21
3	Metal Furn. & Fix.	MPWH	132.4	19.5	0.147	11.00	1.62
4	Containers & Closures	MPWH	94.6	15.3	0.162	26.00	4.21
5	Sheet, Strip & Coil	MPWH	53.1	8.6	0.162	10.00	1.62
6	Appliances	MPWH	180.2	4.7	0.026	5.00	0.13
7	Automotive	MPWH	7,817.0	186.0	0.024	14.50	0.35
8	Trucks and Buses	MPWH	41.3	3.7	0.090	3.00	0.27
9	Railroad	MPWH	38.5	N/A	0.000	1.50	0.00
10	Aircraft	MPWH	578.3	125.1	0.216	1.50	0.32
11	Machinery & Equipment	MPWH	1,979.3	191.2	0.097	9.00	0.87
12	Electrical Insulation	MPWH	253.5	13.5	0.053	1.00	0.05
13	Marine	MPWH	323.0	35.3	0.109	4.00	0.44
14	Paper, Film, & Foil	MPWH	53.1	8.6	0.162	3.00	0.49
15	Other Prod. Finishes	MPWH	53.1	8.6	0.162	15.00	2.43
16	Int. Archit. Coatings	SFH	65,742	7,201	0.110	17.00	1.86
17	Ext. Archit. Coatings	1000 persons	234,023	25,186	0.108	8.60	0.93
SPECIAL PURPOSE COATINGS							
18	Auto Refinishing	1000 autos	130,364	14,274	0.109	7.00	0.77
19	Maintenance	c				4.00	0.48
20	Aerosol	c			0.104	0.00	0.00
21	Traffic Paints	1000 mi roads	3,891	173	0.044	0.00	0.00
22	Other	c				12.00	1.36
23	Thinner & Misc.	c				74.00	8.72
TOTALS							
Industrial						235.10	27.71
Consumer						209.50	24.92
						25.60	2.79

^aData sources for apportionment parameters:

MPWH (million production worker hours) -
 SFH (single family homes) - U.S. Department of Housing and Urban Development (Shoun, 1986)
 1000 persons - U.S. Bureau of the Census (Nerby, 1985)
 1000 registered autos - U.S. Federal Highway Administration (1984)
 1000 miles public roads - Motor Vehicle Manufacturers Association (Baker, 1985)

^bConnolly et al. (1982).

^cSee Rogozen et al. (1985) for method of apportionment in these categories.

Summing emissions from each of the three glycol ethers, we estimate that 10,950 tons of these compounds are emitted to the California atmosphere annually.

16.4.2 National Paint and Coatings Association Data

The National Paint and Coatings Association (Connolly et al., 1982) gathered data on glycol ether solvent use in product finishes, architectural coatings, other special purpose coatings, and paints and finishes (Table 16.4-1). Depending upon the product category, SAIC used the California-to-U.S. ratio of either million worker production hours or population to apportion U.S. usage to California. We found that industrial use of glycol ethers in California was 24.9 million pounds (12,450 tons) in 1981. Assuming this entire amount is volatilized, 12,450 tons of glycol ethers were emitted by industrial users of paints and coatings.

Based upon SAIC survey data, we calculated total emissions of glycol ethers from all sources to be approximately 11,000 tons/yr. From NPCA data we calculated emissions from all paint and coating uses to be 12,450 tons/yr. This figure undoubtedly covers most solvent uses for the glycol ethers. These two numbers compare very favorably, especially when considering the fact that the SAIC survey data does not include industrial uses of product formulations which contain EGMME.

16.5 CONSUMER USE AND EMISSIONS

All three glycol ethers are used as diluents or as anti-icing additives in brake fluids. EGMME and EGME are used as anti-stall agents in gasoline. They may be present in varnish removers, thinners, cleaning products, soaps, detergents, cosmetics, pesticides, pharmaceuticals, and adhesives. EGMBE is also used as a solvent in liquid household cleaners, rust removers, insecticides and herbicides (USDHHS, 1983). Ethylene glycol ethers have largely been replaced by propylene glycol ethers in consumer paints (Trehitt and Bluestone, 1985).

As mentioned in Section 16.4, the National Paint and Coatings Association (Connolly et al., 1982) gathered data on glycol ether solvent use in product finishes, architectural coatings, other special purpose coatings, and paints and finishes in the U.S. in 1981 (Table 16.4-1). From these data, we calculated that California consumers used 2.8 million pounds (1,400 tons) of glycol ethers in 1981. Again, we assumed that the entire amount volatilizes; therefore, this figure represented the portion of glycol ethers emitted by consumer use of paints and coatings.

Emissions of glycol ethers by consumer products may also be calculated from SAIC survey data (Rogozen et al., 1985). Using emissions of EGMBE and EGME from industrial and consumer product use, and a consumer/industrial use ratio of 0.10 (from Table 16.4-1), we calculated emissions of 1,050 tons/yr. This figure does not include EGME emissions from consumer products since such data were not reported. Nonetheless, it is very similar to the 1,400 tons calculated previously from NPCA data. Emissions from consumer products which have been formulated outside California are not included in these totals.

The precise amounts of glycol ethers in other consumer products varies from product to product and from year to year. To date no statewide inventory exists which lists such consumer items, reports the proportional content of glycol ethers in each, and estimates total glycol ether emissions to the atmosphere. Such an undertaking would be fraught with difficulty because of the plethora of company brand names, variation of formulas across brands as well as within brands, and continual changing of brand contents over time.

16.6 EMISSION SUMMARY

Glycol ethers are not produced within California. No indirect pathways to the formation of glycol ethers appear to exist either. A variety of industrial products, such as additives to fuels and solvents in protective coatings, printing inks, and leather dyes, use glycol ethers. Consumer products which may contain glycol ethers include gasoline, brake fluids, insecticides, detergents, cosmetics, adhesives, and liquid household cleaners. We estimated that direct industrial use accounts for over 4,950 tons/yr of

EGMBE, and over 5,750 tons/yr of EGME. We also estimated that approximately 200 tons/yr of EGME are released by direct industrial use, but are unable to estimate industrial and consumer emissions from products which contain this compound. Annual California emissions of these three glycol ethers from industrial uses is approximately 11,000-12,450 tons/yr. Annual emissions from consumer products are 1,450 tons. Thus, total California emissions of these glycol ethers is between 12,400 and 13,850 tons/yr.

16.7 SUMMARY OF AMBIENT CONCENTRATION DATA

No data are available regarding ambient levels of glycol ethers, $\text{CH}_2\text{OH}-\text{CH}_2\text{OR}$, including ethylene glycol methyl ether ($\text{R}=\text{CH}_3$), ethyl ether ($\text{R}=\text{CH}_2\text{CH}_3$) and n-butyl ether ($\text{R}=\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

16.8 ATMOSPHERIC CHEMISTRY

16.8.1 In-Situ Formation

There are no known reactions that would lead to the in-situ production of glycol ethers in the atmosphere.

16.8.2 Removal Processes

There are no experimental kinetic or product data for reactions of glycol ethers that may be relevant to their removal in the atmosphere. We estimate photolysis, reaction with O_3 and reaction with NO_3 to be of negligible importance. Removal of glycol ethers from the atmosphere will involve their reaction with the hydroxyl radical. Estimated OH reaction rate constants are given in Table 16.8-1 for ethylene glycol methyl, ethyl and n-butyl ethers. The first set of estimates in the table is derived from structure-reactivity relationships (see Chapter 3). The second set of estimates is obtained by applying Greiner's formula to OH-abstractable hydrogen atoms from alkanes and ethers:

$$k_{\text{OH}} = N_1 k_1 + N_2 k_2$$

where N_1 and N_2 are the number of primary and secondary hydrogen atoms and k_1 and k_2 are the corresponding OH reaction rate constants per C-H bond:

$$k_1 = 6.4 \times 10^{-14} \text{ (alkanes) or } 6.0 \times 10^{-13} \text{ (ethers)}$$
$$k_2 = 5.6 \times 10^{-13} \text{ (alkanes) or } 1.7 \times 10^{-12} \text{ (ethers)}$$

in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. As is seen in Table 16.8-1, the two sets of estimates are in reasonable agreement.

Tentative mechanisms are given in Figures 16.8-1, 16.8-2 and 16.8-3 for the reactions of OH with ethylene glycol methyl ether, ethyl ether and n-butyl ether, respectively. These mechanisms obviously involve identical pathways for the three glycol ethers (and for that matter, for all ethylene glycol n-alkyl ethers).

The initial OH attack involves H-atom abstraction from the C-H bonds (abstraction from the strong O-H bond in the primary alcohol group $-\text{CH}_2\text{OH}$ is negligible). The major pathways will involve secondary H-atom abstraction from the weaker ether C-H bonds and to a lesser extent from the alkyl chain C-H bonds. The relative importance of these pathways can be roughly estimated from the rate constants per C-H bond given above: abstraction from ether C-H bonds accounts for 54, 70, and 57 percent of the total OH-glycol ether reaction for the methyl, ethyl and n-butyl ethers, respectively.

Reactions of the alkoxy radicals will involve reaction with O_2 and unimolecular decomposition, the latter involving both C-C and C-O bond scission. The relative importance of these three pathways is not known. For ethylene glycol methyl ether (Figure 16.8-1), the expected products of the major abstraction path are hydroxymethyl acetate, $\text{CH}_2\text{OHCOOCH}_3$ (O_2 abstraction), CH_3OCHO (C-C bond scission) and CH_2OHCHO (C-O bond scission). Further reactions of the aldehydes CH_3OCHO and CH_2OHCHO with OH lead to formaldehyde, carbon dioxide, and the peroxy nitrates RC(O)OONO_2 ($\text{R} = \text{CH}_3\text{O}$ and CH_2OH , respectively). Products of the minor abstraction path are $\text{CH}_3\text{OCH}_2\text{COOH}$, formic acid, and formaldehyde.

Table 16.8-1
ESTIMATED OH-GLYCOL ETHER REACTION
RATE CONSTANTS

(k_{OH} in $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)

Compound	Structure	From Structure-Reactivity Relationship (Chapter 3)	From Greiner's Formula (see text)
Ethylene glycol, methyl ether	$\text{HOCH}_2\text{CH}_2\text{OCH}_3$	1.1×10^{-11}	0.63×10^{-11} [a]
Ethylene glycol, ethyl ether	$\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$	1.6×10^{-11}	0.97×10^{-11} [b]
Ethylene glycol, n-butyl ether	$\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	2.1×10^{-11}	1.19×10^{-11} [c]

^a Assume 2 secondary H (ether), 2 secondary H (alkane) and 3 primary H (ether).

^b Assume 4 secondary H (ether), 2 secondary H (alkane) and 3 primary H (alkane).

^c Assume 4 secondary H (ether), 6 secondary H (alkane) and 3 primary H (alkane).

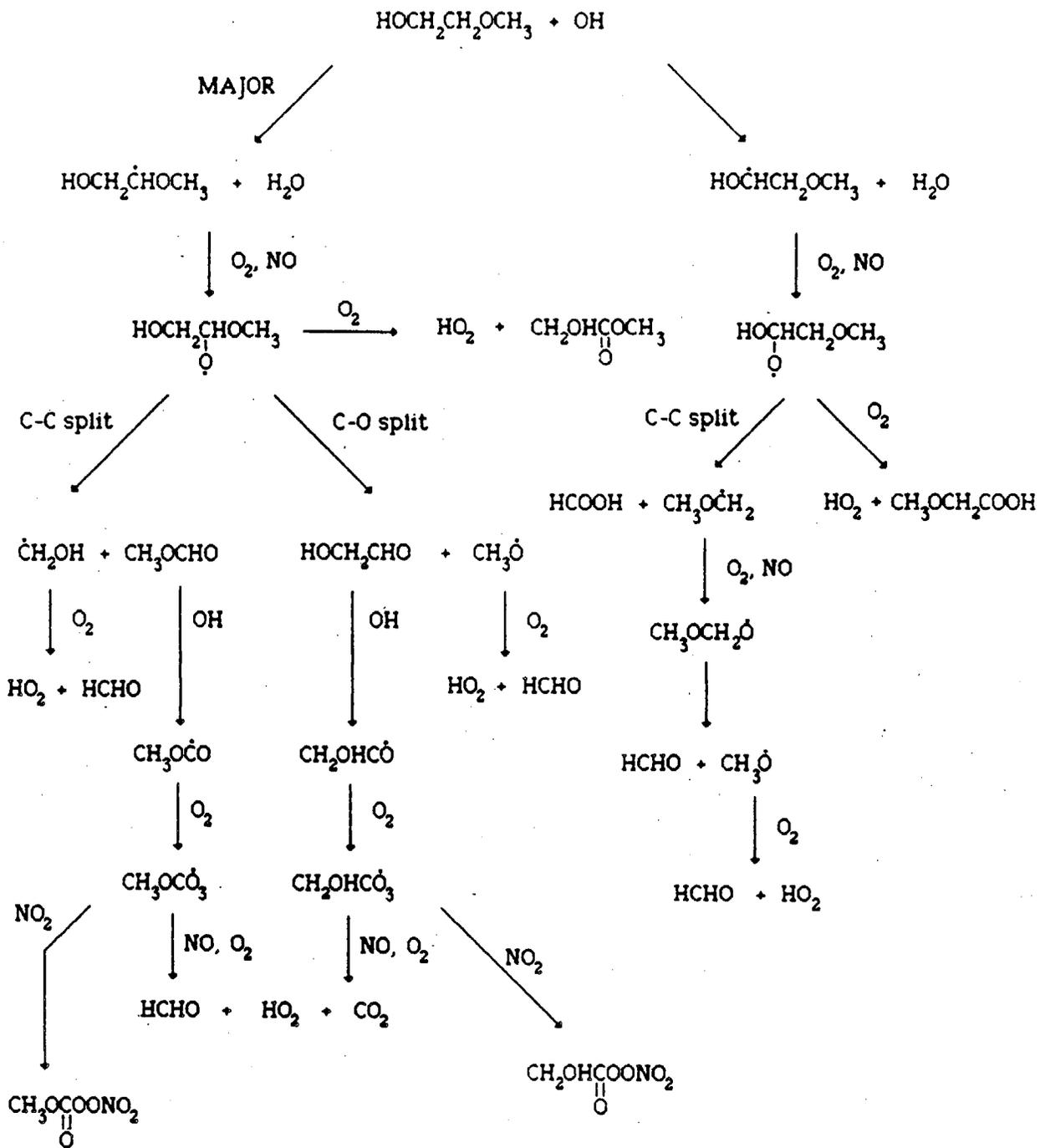


Figure 16.8-1. OH-Ethylene Glycol Methyl Ether Reaction.

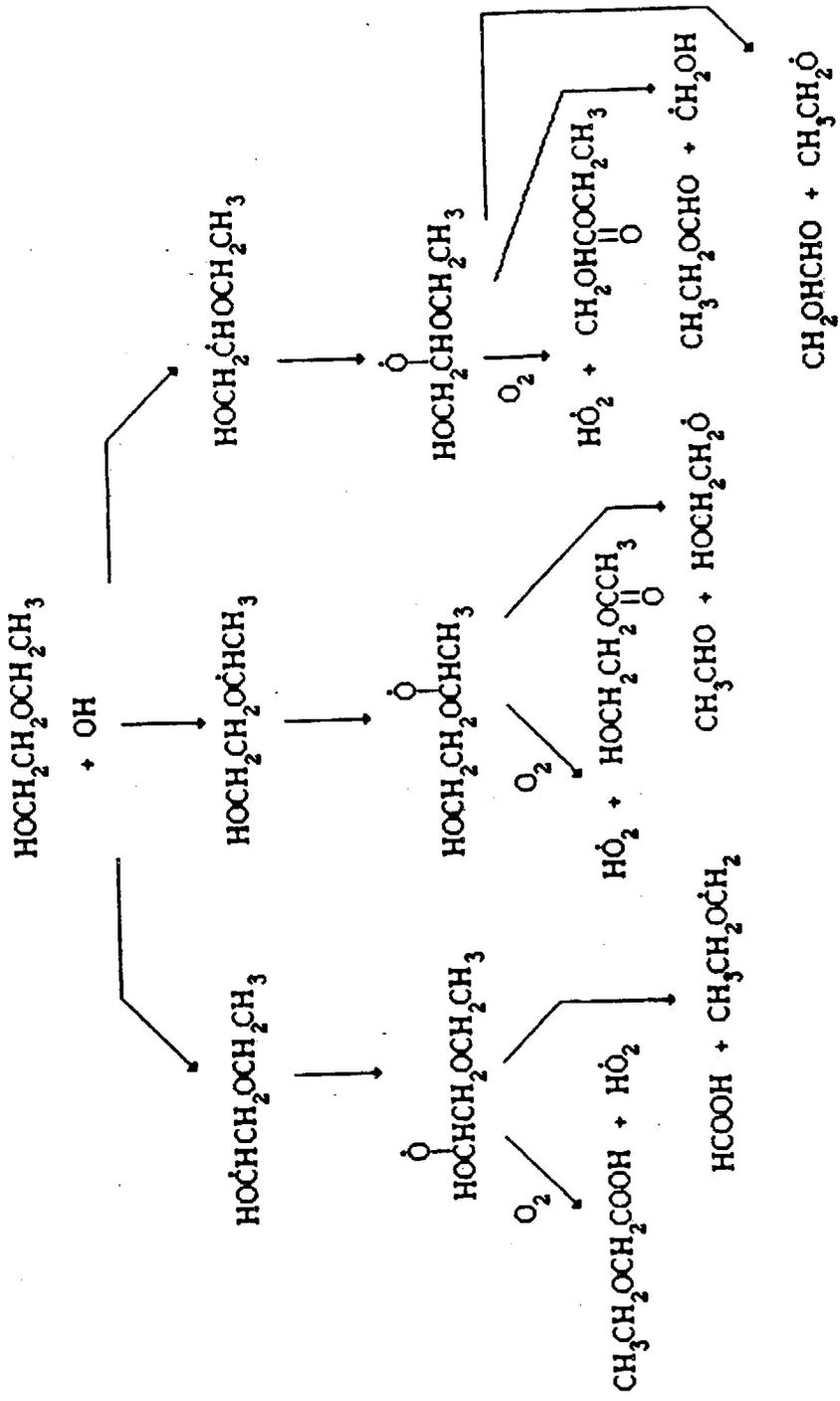


Figure 16.8-2. OH-Ethylene Glycol Ethyl Ether Reaction.

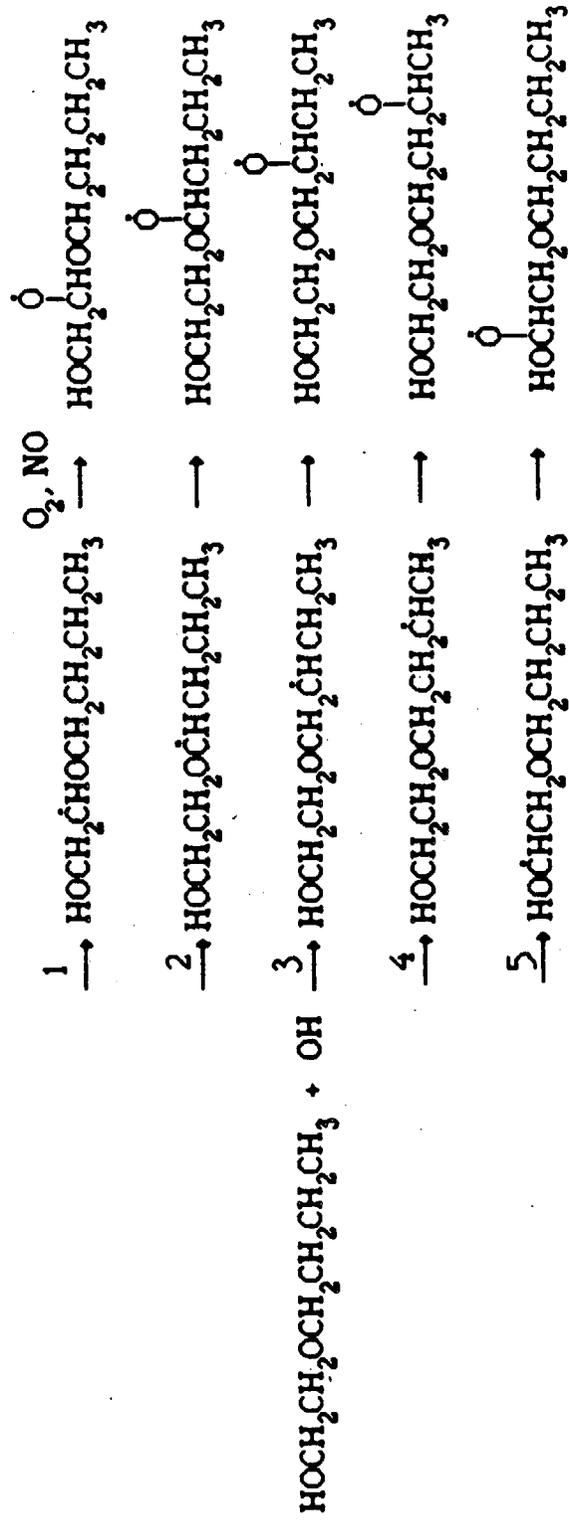


Figure 16.8-3. OH-Ethylene Glycol n-Butyl Ether Reaction.

The reaction of OH with ethylene glycol ethyl ether involves three abstraction sites instead of only two for the methyl ether (Figure 16.8-2). Further reactions of the three alkoxy radicals are identical to those described for the methyl ether and involve reaction with O_2 by abstraction and unimolecular decomposition involving C-C and C-O bond scission as appropriate. Expected products include ethyl hydroxyacetate ($CH_2OHCOOCH_2CH_3$), hydroxyethyl acetate ($CH_3COOCH_2CH_2OH$), ethoxyacetic acid ($CH_3CH_2OCH_2COOH$), formic acid ($HCOOH$), and several aldehydes and free radicals. Further reactions of the aldehydes with OH (not shown in Figure 16.8-2 for clarity) are expected to be identical to those shown in Figure 16.8-1 for the aldehyde products of the OH-ethylene glycol methyl ether reaction.

The reaction of OH with ethylene glycol n-butyl ether may involve five reaction sites. Since C-H bonds in ethers are slightly weaker than C-H bonds in alkanes, the OH reaction is expected to proceed preferentially according to the pathways indicated as 1 and 2 in Figure 16.8-3. Further reactions of the five alkoxy radicals, not shown in Figure 16.8-3, involve reaction with O_2 by abstraction and unimolecular decomposition involving C-C and C-O bond scission. Subsequent reactions of the first generation products are expected to be identical to those shown in Figure 16.8-3 for ethylene glycol methyl ether.

16.9 REFERENCES

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EVALUATION OF HEXACHLOROCYCLOPENTADIENE

17.1 PHYSICAL AND CHEMICAL PROPERTIES

Hexachlorocyclopentadiene is a dense oily liquid. Table 17.1-1 summarizes some of its physical and chemical properties.

17.2 DIRECT PRODUCTION IN CALIFORNIA

Velsicol Chemical Corporation is the only company manufacturing hexachlorocyclopentadiene in the United States in commercial quantities. None is manufactured in California (Levin, 1985).

17.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

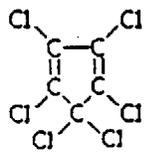
To the best of our knowledge there is no mechanism for indirect production of hexachlorocyclopentadiene.

17.4 INDUSTRIAL USE AND EMISSIONS

Hexachlorocyclopentadiene is used to produce the flame retardants chlorendic anhydride and chlorendic acid. It is also used as an intermediate in the production of pesticides such as aldrin, dieldrin, endosulfan, mirex, and kepone. Occupational exposures appear to constitute the only documented source of human exposure to hexachlorocyclopentadiene (Sittig, 1981).

Although many of the chlorinated hydrocarbons which are manufactured using hexachlorocyclopentadiene are banned for general use, some of these compounds are still registered with the California Department of Food and Agriculture (DFA) for use in limited quantities. According to the DFA, there are 5 active registered labels for aldrin, 1 for dieldrin, and 35 for chlordane. Mirex and kepone are not actively registered in California (Hansen, 1985). We spoke with all of the distributors of aldrin and dieldrin, and some of the distributors of chlordane, to discover what the actual distribution of

Table 17.1-1
CHEMICAL DATA SUMMARY FOR HEXACHLOROCYCLOPENTADIENE

Property	Value for Hexachlorocyclopentadiene
CAS Registry No.	77-47-4
Synonyms	Perchlorocyclopentadiene, C-56, HCCPD
Molecular Weight	272.77
Molecular Formula	C ₅ Cl ₆
Molecular Structure	
Physical State at STP.	Dense, oily liquid
Boiling Point	239 ^o C
Melting Point	-11.34 ^o C 9 ^o C ^a
Specific Gravity	
at 20 ^o C	1.710
at 25 ^o C/4 ^o C ^a	1.702
Vapor Pressure	
at 25 ^o C	0.08 mm Hg
at 62 ^o C	0.975 mm Hg
Vapor Density (air=1)	9.4
Solubility	2.1 mg/L at 25 ^o C
Log Partition Coefficient (octanol/H ₂ O)	5.04
Henry's Law Constant	2.7 x 10 ⁻² atm-m ³ /mole

Source: Hunt and Brooks (1984), unless otherwise noted.

^a SAI (1980).

these compounds in California was, and to trace their production to the manufacturers.

For aldrin and dieldrin, several of the products listed as registered by the DFA are no longer actually registered in the state and the remainder are not actively distributed (McDowell, 1986; McQuerry, 1986; Strong, 1986). Distributors generally retain the registrations even though they are unused, because it is difficult to get a new compound registered in California (Strong, 1986).

A representative from the Velsicol Chemical Company (Levin, 1985), which is the sole manufacturer of hexachlorocyclopentadiene in the United States, stated that, with the exception of one very small order, Velsicol has not shipped any of the compound into California. A toxic air pollutant emission inventory prepared for the U.S. Environmental Protection Agency, Region IX (Bloomhardt and Pelland, 1985) lists Zoecon of Palo Alto as a user of hexachlorocyclopentadiene. However, a representative of this company told SAIC that it does not use the compound (Van den Bosch, 1986). No flame retardants are manufactured in California (Bloomhardt and Pelland, 1985).

Considering all of the above evidence, it appears as if there are no emissions into the air from the use of hexachlorocyclopentadiene in the production of other compounds in California.

17.5 CONSUMER USE AND EMISSIONS

Production and use of hexachlorocyclopentadiene is limited to the few manufacturers mentioned in Section 17.4. No consumer use exists for this compound.

17.6 EMISSION SUMMARY

It is highly unlikely that hexachlorocyclopentadiene is emitted into the California ambient air. The only manufacturer, Velsicol, neither produces the compound in California nor ships it into the state. The only industrial uses are as intermediates in the manufacturing of flame retardants and

chlorinated hydrocarbon pesticides. It appears that this type of industrial activity does not take place in California.

17.7 SUMMARY OF AMBIENT CONCENTRATION DATA

No data are available regarding ambient or near-source levels of hexachlorocyclopentadiene in air.

17.8 ATMOSPHERIC CHEMISTRY

17.8.1 In-Situ Formation

There are no known reactions that could lead to in-situ formation of hexachlorocyclopentadiene in the atmosphere.

17.8.2 Removal Processes

There have been no experimental studies of the kinetics and products of reactions that may be relevant to the removal of hexachlorocyclopentadiene in the atmosphere.

Removal by photolysis may be important but has not been studied. Our structure-reactivity relationship estimates (Chapter 3) indicate that hexachlorocyclopentadiene is very reactive towards the hydroxyl radical, the nitrate radical, and ozone:

$$\begin{aligned}k_{OH} &\sim 9.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \\k_{O_3} &\sim 4.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \\k_{NO_3} &\sim 2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\end{aligned}$$

Independent empirical estimates can be arrived at for k_{OH} by comparing the effect of chlorine atom substitution in ethylene (kinetic data are available for chloroethenes) to that expected for cyclopentadiene, for which no data exist. Kinetic data for relevant compounds are compiled in Table 17.8-1. They indicate that the reaction rate constants estimated from structure-reactivity relationships are consistent with those expected from chlorine atom

Table 17.8-1
EFFECT OF CHLORINE ATOM SUBSTITUTION AT THE REACTION
CENTER ON THE REACTIVITY OF OLEFINS TOWARDS OH

Compound	Structure	$k_{OH}, \text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$	k_{OH} , relative to ethylene
Ethylene	$\text{CH}_2 = \text{CH}_2$	8×10^{-12}	1.0
Vinyl chloride	$\text{CH}_2 = \text{CHCl}$	6.6×10^{-12}	0.825
1,1-Dichloroethene	$\text{CCl}_2 = \text{CH}_2$	6.5×10^{-12}	0.812
Cis-1,2-dichloroethene	$\text{CHCl} = \text{CHCl}$	2.0×10^{-12}	0.250
Trans-1,2-dichloroethene	$\text{CHCl} = \text{CHCl}$	4.5×10^{-12}	0.562
Trichloroethene	$\text{CHCl} = \text{CCl}_2$	2.4×10^{-12}	0.300
Tetrachloroethene	$\text{CCl}_2 = \text{CCl}_2$	0.17×10^{-12}	0.021
1,3-Cyclopentadiene		no data	-
1,3-Cyclohexadiene ^a		156×10^{-12}	19.5
Hexachlorocyclohexadiene ^b		93×10^{-12}	11.6

^aClose structural homologue of cyclopentadiene.

^b k_{OH} estimated from structure-reactivity relationships.

substitution at the C=C reaction center.

Tentative mechanisms are outlined in Figure 17.8-1 for the OH reaction and in Figure 17.8-2 for the ozone reaction. These mechanisms are consistent with those for the reactions of OH and O₃ with simple olefins and diolefins. Addition of OH may take place at the C₁ and C₂ carbon atoms, leading to the unsaturated dichloride ClCOC(Cl)=CClCCl₂COCl. This compound may photolyze and react with OH to yield ClCOCOC(Cl) and ClCOC(Cl)₂COCl. These carbonyl chlorides presumably photolyze (their reactions with OH, O₃, etc. are deemed negligible) to yield CO, ClO₂ radicals and other products. Addition of ozone (Figure 17.8-2) leads to two unsaturated Criegee biradicals. Rearrangement of these biradicals to carboxylic acids is not possible since they contain no hydrogen atoms, and their further reactions may involve fragmentation to CO₂, chlorine atoms and unsaturated fragments. Reactions may involve fragmentation to CO₂, chlorine atoms and unsaturated fragments. Reactions of the unsaturated fragments with OH and with O₃ will in turn lead to ClCOC(Cl), ClCOC(Cl)₂COCl, and other chlorine-containing products. Comparison

$\begin{array}{ccc} \text{O} & & \text{O} \\ \parallel & & \parallel \\ \text{O} & & \text{O} \end{array}$

with structural analogues containing fewer chlorine atoms (e.g. see Chapter 7, allyl chloride, and Chapter 27, vinylidene chloride) suggest that the products of atmospheric reactions of hexachlorocyclopentadiene may be of high toxicity.

17.9 REFERENCES

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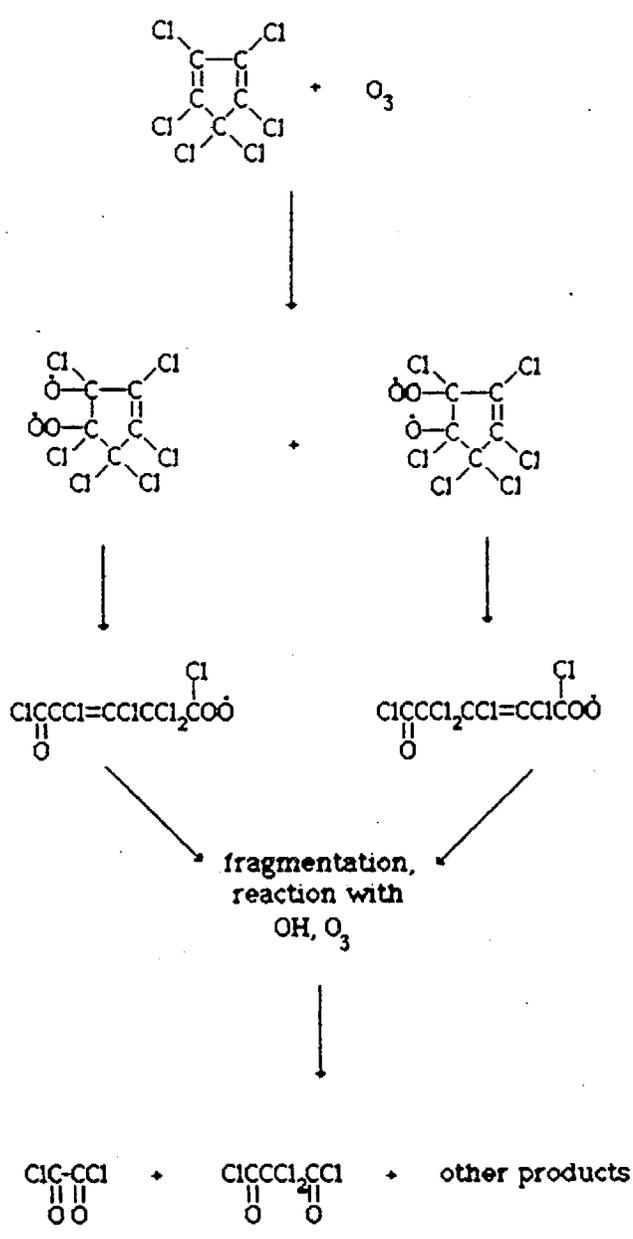


Figure 17.8-2. Ozone-Hexachlorocyclopentadiene Reaction.

Strong, L. 1986. Personal communication from Product Administrative Supervisor, J.R. Simplot Co., Lathrop, CA (14 January).

Van den Bosch, T. 1986. Personal communication from Zoecon, Palo Alto, CA (13 February).

18.0

EVALUATION OF MALEIC ANHYDRIDE

18.1 PHYSICAL AND CHEMICAL PROPERTIES

Maleic anhydride is a solid which has the shape and color of white needles or flakes. Table 18.1-1 summarizes some of its physical and chemical properties.

18.2 DIRECT PRODUCTION IN CALIFORNIA

The maleic anhydride industry has undergone several changes in the last six years, as some plants have been closed, one has opened, and several have changed from benzene to butane feedstock. At present six companies produce maleic anhydride (MA) at eight plants, none of which is in California (Anon., 1982, 1983a, 1983b; USEPA, 1980).

18.3 INDIRECT PRODUCTION AND EMISSIONS

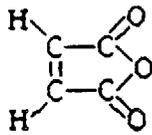
To the best of our knowledge, the only indirect source of maleic anhydride emissions occurs when MA is formed as a side reaction during the manufacturing of phthalic anhydride (Patterson et al., 1976). Phthalic anhydride was formerly produced by Chevron Chemical Company in Richmond and by Allied Corporation in El Segundo. Both of these facilities ceased production of phthalic anhydride several years ago, however (Lyon, 1986; Pon, 1986); therefore indirect production and emissions of MA from this source do not occur in California.

18.4 INDUSTRIAL USE AND EMISSIONS

18.4.1 Use in California

About 52 percent of the maleic anhydride available for consumption in 1981 in the U.S. was used to manufacture unsaturated polyester resins (SRI, 1981). A much smaller, although unspecified, amount was used in producing alkyd resins; the latter are polyester resins formed from polyhydric alcohols,

Table 18.1-1
CHEMICAL DATA SUMMARY FOR MALEIC ANHYDRIDE

Property	Value for Maleic anhydride
CAS Registry No.	108-31-6
Synonyms	(cis) butenedioic anhydride; 2,5-furandione; toxilic anhydride
Molecular Weight	98.06
Molecular Formula	(CHCO) ₂ O
Molecular Structure	
Physical State at STP	White needles or flakes
Boiling Point	199.7/202°C
Melting Point	53°C
Specific Gravity	
Vapor Pressure	0.00005 mm @ 20°C, 0.0002 mm @ 30°C
Vapor Density (air=1)	3.38
Solubility	
Log Partition Coefficient (octanol/H ₂ O)	
Henry's Law Constant	

Source: SAI (1980).

polybasic acids and fatty acids. Normally, phthalic anhydride is used as the polybasic acid. However, in some cases maleic anhydride may replace up to 10 percent of the phthalic anhydride on a molar basis (Wilkins, 1977). Other nationwide uses of MA include chemical intermediate for lube oil additives (12 percent), fumaric acid (11 percent), agricultural chemicals (9 percent), and malic acid (4) percent; comonomer for other copolymers (5 percent); and other uses (7 percent) (SRI, 1981).

To the best of our knowledge, the only significant uses of MA in California are in production of unsaturated polyester resins and alkyd resins. Through searches of the chemical directories and data bases mentioned in Section 3.2.1, SAIC identified 27 California firms which were potential users of maleic anhydride. All were contacted by telephone, and follow-up letters were sent to known users. Table 18.4-1 lists the facilities which told SAIC that they used maleic anhydride for at least one of those types of resin. Uses which could not be confirmed as of this writing are indicated with a question mark. The list is probably not exhaustive. For example, the emissions data compilations to be presented in Section 18.4.2 include several additional facilities. However, we believe that the facilities shown in Table 18.4-1 represent the great majority of the maleic anhydride use in the state.

Information on maleic anhydride use was obtained through telephone calls and letters to the listed firms. In addition, the Society of the Plastics Industry, Inc. (SPI), as a courtesy to SAIC, employed Ernst and Whinney to survey 12 unsaturated polyester manufacturers regarding their maleic anhydride use in California (Guyon, 1986). Seven of the companies in the SPI survey reported using MA in the state. In keeping with trade secret preservation requirements, only the summary results of the SPI survey and SAIC's information requests may be presented:

	<u>Use in 1984 (1b)</u>	<u>Use in 1985 (1b)</u>
Unsaturated Polyester Resin	36,756,608	36,549,276
Alkyd Resins	24,875	20,628
Both (apportionment unknown)	<u>500</u>	<u>500</u>
Total Use	36,781,983	36,570,404

Table 18.4-1

USERS OF MALEIC ANHYDRIDE AS FEEDSTOCK FOR UNSATURATED
POLYESTER AND ALKYD RESINS IN CALIFORNIA, 1984-1985

Facility	City	County	Unsaturated Polyester Resin	Alkyd Resins
Alpha Corporation	Perris	Riverside	x	
Ashland Chemical Company	Los Angeles	Los Angeles	x	x
Cargill, Inc.	Lynwood	Los Angeles	x	x?
Cook Paint and Varnish Company	Milpitas	Santa Clara	x? ^a	x?
Fuller-O'Brien Corporation	S. San Francisco	San Mateo		x?
Glidden Coatings and Resins Div. of SCM	San Francisco	San Francisco		x ^c
Hugh J. Resins Company	Long Beach	Los Angeles	x?	x
Inmont Corporation	Anaheim	Orange	x?	
Kelly-Moore Paint Company	San Carlos	San Mateo		x ^b
Koppers Company, Inc.	Richmond	Contra Costa	x	
	Oxnard	Ventura	x	
McCloskey Corporation	Los Angeles	Los Angeles	x?	
Reichhold Chemicals, Inc.	Azusa	Los Angeles	x	x
Sherwin-Williams	Emeryville	Alameda		x
Silmar Division of Sohio	Hawthorne	Los Angeles	x	
U.S.S. Chemicals Div. of U.S. Steel	Colton	San Bernardino	x	x

^a? means use of maleic anhydride for this product is unconfirmed.

^bUse of maleic anhydride to be discontinued in 1986.

^cNo use of maleic anhydride in 1985.

Actual use is likely to be higher, since (1) several of the firms contacted by SPI and SAIC did not provide the requested information and (2) as noted above, other maleic anhydride users have evidently been identified by the South Coast and Bay Area air quality management districts.

18.4.2 Emission Estimates

Although maleic anhydride is a solid at ambient temperatures, it sublimates at the temperatures typical of unsaturated polyester resin and alkyd resin reactors, which are 210 - 280°C and 440°C, respectively (Wilkins, 1977). Thus, one would expect the main sources of emissions to be venting or fugitive releases from reactor kettles (EPA source classification code 3-01-018-38). Emissions from the other two sources for which the EPA has source classification codes (resin thinning and resin storage) would be negligible, since most of the MA would have taken part in the resin formation reactions, and the temperature of any unreacted MA would be below the compound's sublimation point. Unfortunately, no emission factors for this source have been published. In calculating emissions from maleic anhydride users responding to the South Coast Air Quality Management District's toxic air pollutant survey (Zwiacher et al., 1983), the District used emission factors ranging from 0.05 to 0.25 lb/ton of maleic anhydride used. From data reported by one respondent, an emission factor of about 4.5 lb per ton can be derived. Applying this wide range of emission factors to the statewide maleic anhydride use reported in Section 18.4.1 yields an estimate of 0.45 to 41 tons (0.41 to 37 MT) in 1985.

Table 18.4-2 summarizes the emission estimates published by the SCAQMD (Zwiacher et al., 1983) and the Bay Area Air Quality Management District (Hill, 1985). Total emissions from these sources are 8.0 tons (7.3 MT) per year. To the best of our knowledge, there is only one potential MA source outside the two major districts, and its emissions are probably relatively small.

Table 18.4-2

MALEIC ANHYDRIDE EMISSIONS ESTIMATED BY SOUTH COAST AND
BAY AREA QUALITY MANAGEMENT DISTRICTS

Firm	City	County	Emissions		BAAQMD kg/yr
			SCAQMD 1b/yr	kg/yr	
Alpha Resins	Perris	Riverside	6,000	2,721.1	-
Ampex Corporation	San Mateo	San Mateo			a
Ashland Chem. Corp.	Los Angeles	Los Angeles	130	59.0	-
Cargill Inc.	Lynwood	Los Angeles	285	129.3	-
Celanese Plastics & Specialties	Los Angeles	Los Angeles	6	2.7	-
Chevron Chemical Company	Richmond	Contra Costa			
Chevron Research Company	Richmond	Contra Costa			a
Clorox Technical Center	Pleasanton	Alameda			
Cook Paint and Varnish Co.	Milpitas	Santa Clara		3,600	1,640
Coulter Steel & Forge Co.	Emeryville	Alameda			a
DeSoto, Inc	Berkeley	Alameda			
DOE-Sandia National Laboratory	Livermore	Alameda			a
Essex Chemical Corp, Pro-Seal	Compton	Los Angeles	1	0.5	-
Fuller-O'Brien	S. San Francisco	San Mateo			a
Glidden Coatings & Resin	San Francisco	San Francisco		400	180
Hewlett-Packard Co.	Stanford	Santa Clara			a
Hexcel Livermore National Lab	Livermore	Alameda		4,000	1,820
IT Corporation	Martinez	Contra Costa			

Table 18.4-2 (continued)

Firm	City	County	Emissions		BAAQMD kg/yr
			SCAQMD lb/yr	lb/yr	
Kelly-Moore Paint Company	San Carlos	San Mateo			a
Koppers Company, Inc.	Vernon	Los Angeles	2	0.9	-
Koppers Co., Inc	Richmond	Contra Costa			90
Lawrence Livermore National Lab	Livermore	Alameda			a
Lilly Industrial Coating Inc.	Montebello	Los Angeles	1	0.5	-
Litronic Industry	Irvine	Orange	1	0.5	-
McCloskey Varnish Company	Commerce	Los Angeles	9	4.1	-
Pilot Chemical Co. of CA	Santa Fe Springs	Los Angeles	1	0.5	-
PPG Ind., Coatings & Resins Div.	Torrance	Los Angeles	11	5.0	-
Reichhold Chemical Inc.	Azusa	Los Angeles	57	25.9	-
Sherwin-Williams Co.	Emeryville	Alameda			a
Silmar Div., Sohio Chem. Co.	Hawthorne	Los Angeles	375	170.1	-
Tretolite, Div. Petrolite Corp.	Brea	Orange	135	61.2	-
U.S.S. Chem. Polyester Div.	Colton	San Bernardino	264	119.7	-
Union Chemicals Division	Oakland	Alameda			270
Union Oil of CA S/T Div.	Brea	Orange	1	0.5	-
Total			7,279	3,301	8,800
					4,000

^aEmissions could not be estimated but are believed to be less than 0.1 ton/year.

18.5 CONSUMER USE AND EMISSIONS

There are no known consumer uses of maleic anhydride. Emissions from this class of sources are therefore zero.

18.6 EMISSION SUMMARY

The only potential sources of maleic anhydride emissions in California are unsaturated polyester resin and alkyd resin manufacturing plants. Inventoried emissions from these facilities are about 8.0 tons (7.3 MT) per year. This value is highly uncertain, given the lack of established emission factors.

18.7 SUMMARY OF AMBIENT CONCENTRATION DATA

No data are available for maleic anhydride in ambient air, in California or elsewhere.

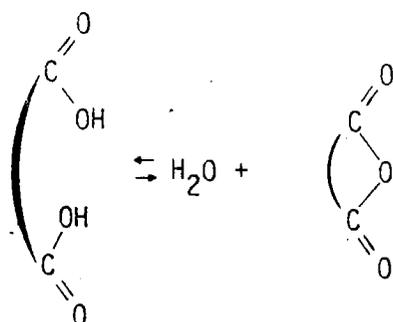
18.8 ATMOSPHERIC CHEMISTRY

18.8.1 In-Situ Formation

In-situ formation of maleic anhydride in the atmosphere may involve the reaction of aromatic hydrocarbons with the hydroxyl radical. Bandow and co-workers (1985) have identified maleic anhydride as a minor product in laboratory studies of the photooxidation of benzene, toluene, and o-xylene, with yields of ≤ 4 percent ± 0.4 percent and 4 ± 1 percent respectively. The authors speculated that maleic anhydride may form by rearrangement of one or more of the "first-generation" aromatic ring opening products, i.e. the aliphatic dicarbonyls. They did not observe maleic anhydride as a product from m-xylene, p-xylene, and several trimethyl benzenes. Other investigators who have studied the atmosphere oxidation of benzene and toluene have not reported maleic anhydride as a reaction product.

A second possible pathway for maleic anhydride formation in the atmosphere may involve loss of water from maleic acid. Anhydrides may form by

loss of water from α,ω -dicarboxylic acids:



The dicarboxylic acid precursor of maleic anhydride is maleic acid, cis-COOH-CH=CH-COOH. No data are available for ambient levels of maleic acid. This compound has occasionally been identified in rainwater samples. It may form by reaction of OH and O₃ with some olefins and some OH-substituted aromatics (e.g. phenols). Thus, in-situ formation of maleic anhydride in the atmosphere is possible but has not been firmly documented at this time.

18.8.2 Removal Processes

There are no data regarding kinetic and product information for reactions of maleic anhydride that may be relevant to its removal from the atmosphere. As an olefin, maleic anhydride is expected to react with OH, O₃ and NO₃. The corresponding reaction rate constants, estimated from structure-reactivity relationships, are as follows:

$$k_{\text{OH}} = 4.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

$$k_{\text{O}_3} = 4.9 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

$$k_{\text{NO}_3} = 6.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Tentative mechanisms are outlined in Figures 18.8-1 and 18.8-2 for the reactions of maleic anhydride with OH and with ozone, respectively. Both reactions involve electrophilic addition on the unsaturated C=C bond, followed

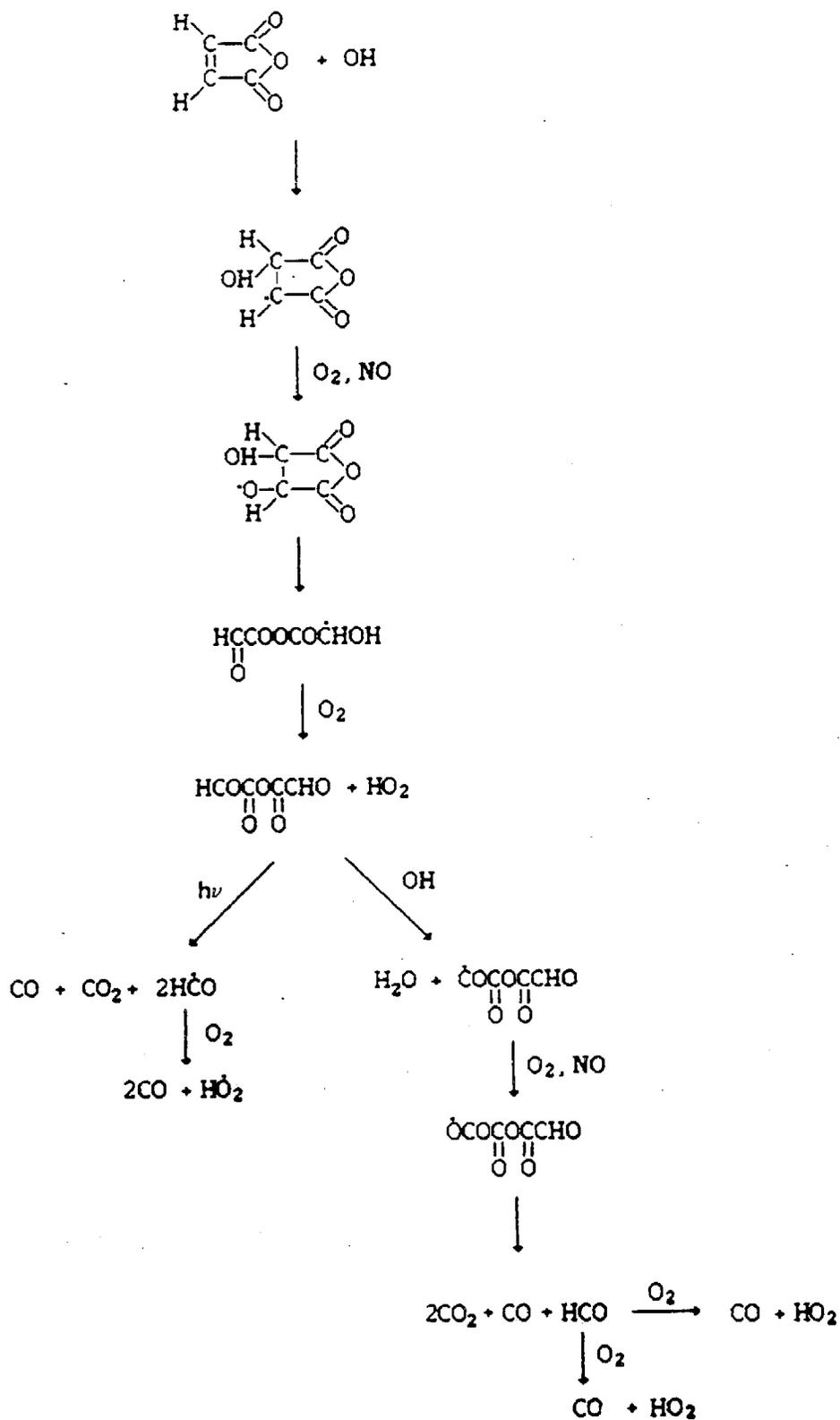


Figure 18.8-1. OH-Maleic Anhydride Reaction.

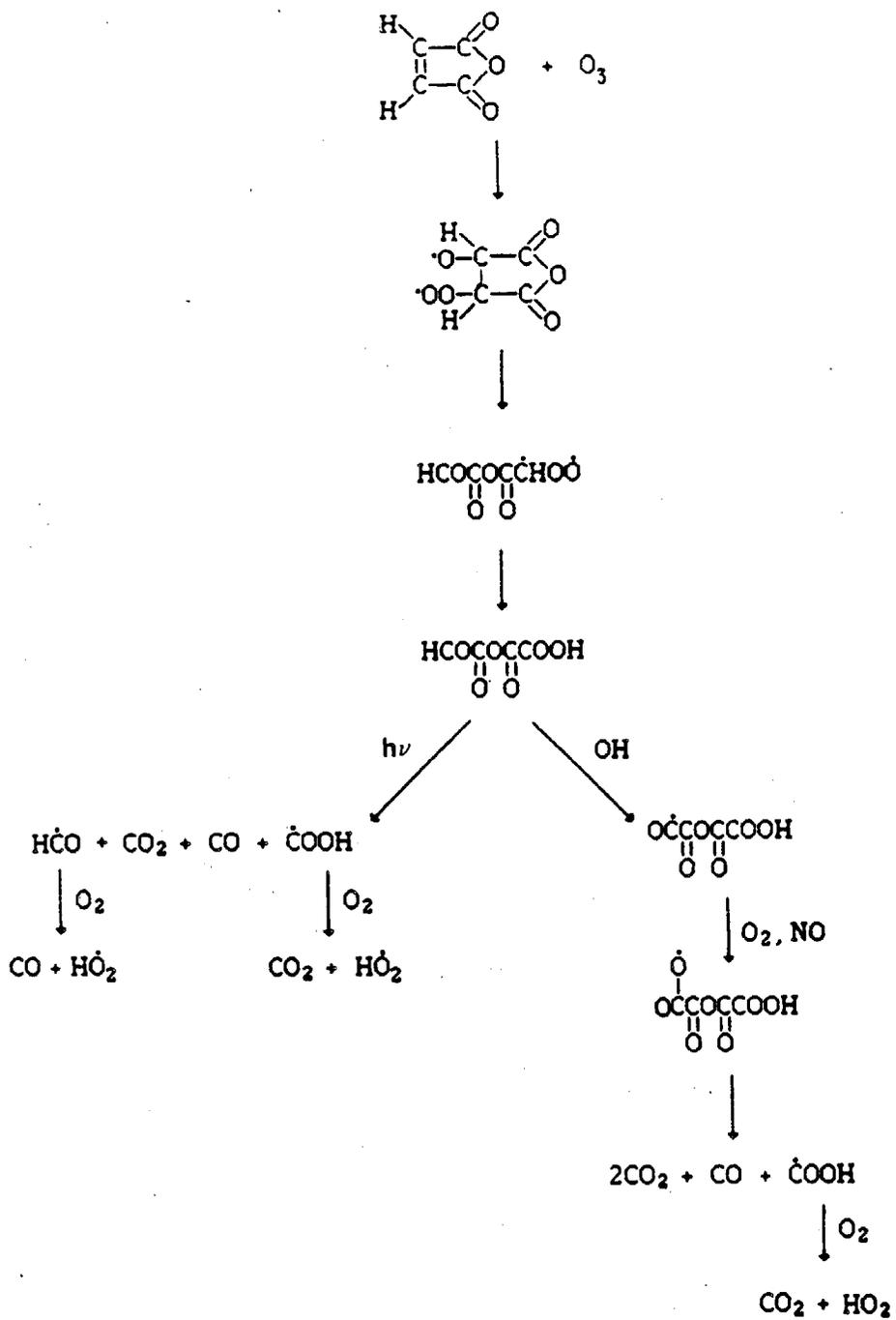


Figure 18.8-2. Ozone-Maleic Anhydride Reaction.

by steps identical to those documented for simple olefins. Reaction with OH leads to the carbonyl HCOCOCCHO , which presumably photolyzes rapidly and

reacts with OH to give CO, CO_2 and HO_2 . Reaction with ozone leads to a similar product, HCOCOCOOH , which is also expected to photolyze rapidly and

to react with OH to give CO, CO_2 and HO_2 . No mechanism is proposed for the reaction of maleic anhydride with NO_3 since the exact mechanism of this reaction is not yet established even for simple olefins. Reactions with OH, O_3 and NO_3 should lead to rapid removal of maleic anhydride from the atmosphere.

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EVALUATION OF MANGANESE

19.1 PHYSICAL AND CHEMICAL PROPERTIES

Elemental manganese is a gray solid. Table 19.1-1 summarizes some of its physical and chemical properties. Although manganese exists in 11 oxidation states from -3 to +7, including 0, the compounds most environmentally and economically important are those containing Mn^{2+} , Mn^{4+} and Mn^{7+} . Some of the properties of these compounds, along with those of the organic compound methylcyclopentadienyl manganese tricarbonyl (MMT), are summarized in Table 19.1-2.

19.2 DIRECT PRODUCTION IN CALIFORNIA

The following discussion is based primarily upon two sources published by the Bureau of Mines (Jones, 1984, 1985). No manganese production exists in California. Manganese ore products, which contain 35 percent or more manganese, have not been produced in the United States since 1970, nor have ferruginous ores, which contain from 10 to 35 percent manganese; ore of this quality is not economically minable at present prices. Table 19.2-1 clearly indicates the declining trend of U.S. manganese production since 1963.

Manganese ores are generally converted to ferromanganese and silicomanganese alloys prior to industrial use. Ferroalloy production totals for 1984 are not reported by the Bureau of Mines because only two producing companies exist; revelation of such figures would disclose proprietary information. The two producers of ferroalloys are Elkem Metals, in Marietta, Ohio; and Chemetals, in Kingwood, West Virginia. In 1982, the last year for which complete production and shipping records for ferromanganese and silicomanganese were publicly available, 119,000 tons of ferromanganese and 69,000 tons of silicomanganese were produced in the U.S.

As Table 19.2-1 indicates, there is a large gap between U. S. domestic manganese consumption needs and U.S. primary production. The

Table 19.1-1

CHEMICAL DATA SUMMARY FOR ELEMENTAL MANGANESE

Property	Value for Elemental Manganese
CAS Registry No.	7439-96-5
Synonyms	
Molecular Weight	54.9380
Molecular Formula	Mn
Physical State at STP	grey-pink metal
Boiling Point	1962 ^o C
Melting Point ^a	1244 ⁺³ ₋₃ ^o C
Specific Gravity ^a	7.2
Vapor Pressure	
Vapor Density (air=1)	
Solubility	Soluble in dilute acids; reacts slowly in hot or cold water.
Log Partition Coefficient (Octanol/H ₂ O)	
Henry's Law Constant	

Source: Weast and Astle (1981), USEPA (1984a).

Table 19.1-2
CHEMICAL DATA SUMMARY FOR MANGANESE COMPOUNDS

Property	MnO	MnO ₂	MnSO ₄	Mn ₃ O ₄
CAS Registry No.	1344-43-0	1313-13-9	7785-87-7	1317-35-7
Synonyms	manganosite	pyrolusite	szmikite, Manganese(II) sulfate, mono hydrate	Manganese (II, III) oxide; hausmannite
Molecular Weight	70.94	86.94	169.01	228.81
Molecular Formula	MnO	MnO ₂	MnSO ₄ · H ₂ O	Mn ₃ O ₄
Molecular Structure				
Physical State at STP	green, cubic crystals	black rhombic crystals or brown black powder	pale pink monoclinic crystals or rhombic	black tetrahedral (rhombic) crystals
Boiling Point	233°C			
Melting Point	1945°C	Decomposes (loses -O @ 535°)	57-117°C stable	1564°C
Specific Gravity	5.43-5.46; 5.37 @ 23°C	5.026	2.95	4.856
Vapor Pressure				
Vapor Density (air=1)				
Solubility	insoluble in H ₂ O soluble in most organic solvents.	insoluble in H ₂ O soluble in acids; NH ₄ Cl	insoluble in H ₂ O, HNO ₃ or acetone; soluble HCl @ 48 g/100 cc or 79.8 g/100 cc @ 100°C	insoluble in H ₂ O; soluble in HCl
Log Partition Coefficient (octanol/H ₂ O)				
Henry's Law Constant				

Source: USEPA (1984a), Meast (1981).

Table 19.2-1
 COMPARISON OF U.S. MANGANESE PRODUCTION AND
 DEMAND, 1960-83
 (Thousand short tons of Manganese Content)

Year	Demand	Production
1963	1,096	94
1964	1,216	79
1965	1,373	83
1966	1,353	88
1967	1,207	73
1968	1,150	48
1969	1,317	93
1970	1,327	66
1971	1,170	38
1972	1,366	29
1973	1,554	31
1974	1,492	35
1975	1,133	19
1976	1,364	31
1977	1,523	27
1978	1,363	38
1979	1,250	31
1980	1,029	23
1981	1,027	24
1982	672	4
1983	668	4

Source: Jones (1985).

majority of this difference is obtained through imports of manganese, manganese ferroalloy, and silicomanganese from approximately 20 countries.

19.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

Elemental manganese and manganese compounds are present in a wide variety of natural and industrial settings. Natural sources include soil, road dust, and burning vegetation; while anthropogenic sources are auto exhaust; combustion of residual oil, distillate, and coal; Kraft and sulfite paper and pulp process combustion; ferromanganese and glass furnaces; asphalt production; rock crushing; and sewage sludge incineration. All these sources are likely to be present in California, although the extent of each activity is not well known. In this section we will discuss emission factors and preliminary estimates of the emissions associated with each of the non-industrial sources. However, precise estimates of California emissions are not possible at this time without further research.

Table 19.3-1 shows the mean concentration of fine and coarse particle fractions of aerosols from various sources, and our judgment as to whether each source is likely to be an air pollution problem in California. As can be seen, the manganese component of emissions from most of these sources is substantially lower than that from electric steel and ferromanganese furnace operations.

19.3.1 Emissions from Sewage Sludge Incineration

Several studies have found manganese in municipal sewage sludge and in particulate emissions from sludge incineration. A survey performed in 1972-1973 found the average manganese content of sludge from 16 cities to be 194 mg/kg dry weight (Furr et al., 1976). Two California wastewater treatment plants submitted sludge samples for analysis. The manganese contents of the Los Angeles Joint Water Pollution Control plant and the Richmond-Sunset wastewater treatment plant in San Francisco were 116 and 113 mg/kg dry weight, respectively. A review of U.S. Environmental Protection Agency (EPA) data by

Table 19.3-1

MANGANESE CONCENTRATION IN FINE (<2.0 μm) AND COARSE (2.0-20 μm)
PARTICLE FRACTIONS OF AEROSOLS FROM SEVERAL SOURCES

Aerosol Source	Mn Concentration (mg/g)		Likely Pollution Problem in California
	Fine Particles	Coarse Particles	
Soil	2.0	0.85	Yes
Road dust	1.23	1.0	Yes
Leaded auto exhaust	0.0 ^a	0.0 ^a	?
Residual oil combustion	0.46	0.46	Yes
Distillate oil	0.14	NR ^b	Yes
Vegetative burn ^c	0.84	0.84	Yes
Kraft recovery boiler	0.3	5.2	Yes
Sulfite recover boiler	0.54	0.54	Yes
Hog fuel boiler	5.1	2.9	?
Aluminum processing	0.11	0.0	No
Steel electric furnace	87	87	Yes
Ferromanganese furnace	173	173	Yes
Carborundum	0.35	0.29	?
Glass furnace	0.021	0.031	Yes
Carbide furnace	0.42	0.36	?
Asphalt production	2.0	NR	Yes
Rock crusher	0.8	NR	Yes
Coal fly ash	0.3	NR	?

Source: USEPA (1984a).

^aDetection limit not reported.

^bNR = Not reported.

^cAverage of two burns.

Gerstle and Albrinck (1982) found mean and median values of 1,190 and 400 mg/kg dry weight, respectively.

Bennett et al. (1984), in tests at four unidentified municipal sludge incinerators, measured the trace elemental composition of the sludge, total particulate emissions, elemental composition of emitted particulate matter, and mass concentrations of the elements in the inlet and outlet of each incinerator's pollution control device. The manganese content of the sludge ranged from 1,100 to 7,000 mg/kg dry weight, i.e. an order of magnitude higher than the values reported by Furr et al. Bennett et al. found that the average enrichment of Mn in the emitted particulate matter (percent Mn in emissions/percent Mn in dry sludge) was 0.61; this would indicate that, compared with other elements, more Mn ends up in the bottom ash and collected scrubber ash, or is volatilized, than is emitted in particulate form. Since the boiling point of manganese is 1962°C (Weast and Astle, 1981), and the highest incinerator temperature measured by Bennett et al. was 879°C, it is unlikely that a significant amount of the manganese is emitted in vapor form. Using data presented by Bennett et al., we calculated manganese emission factors for the four incinerators by dividing Mn emissions by the sludge feed rate. For example, in the case of incinerator "0,"

$$\begin{aligned}\text{Mn emissions} &= \text{Particulate emissions} \times \text{fraction Mn in particulate} \\ &= 1.96 \text{ lb/hr} \times 0.0021 = 0.0041 \text{ lb/hr}\end{aligned}$$

$$\begin{aligned}\text{Emission factor} &= (\text{Mn emissions})/(\text{dry sludge feed rate}) \\ &= (0.0041 \text{ lb/hr})/(11,724 \text{ lb/hr}) \\ &= 3.5 \times 10^{-7}\end{aligned}$$

Emission factors calculated in this way ranged from 9.8×10^{-8} to 3.1×10^{-6} . This large range probably reflects significant differences in sludge composition, incineration methods and conditions, and effectiveness of pollution control equipment. Indeed, the upper bound on the emission factor corresponds to an incinerator whose wet scrubber was able to remove only 77.2 percent of the manganese present in the outlet from the furnace. If this incinerator is removed from consideration, then the range of emission factors becomes 9.8×10^{-8} to 5.2×10^{-7} .

According to the ARB (Woodhouse, 1987), sludge is currently incinerated at seven wastewater treatment plants in California. About 17,000 dry tons of sludge are burned annually. Using the second range of emission factors presented above, we estimate the potential for about 3 to 18 lb/yr of manganese emissions from this source.

19.3.2 Emissions from Fossil Fuel Combustion

19.3.2.1 Coal

According to the ARB, 1.23 million tons of coal were burned in California in 1985 (Nguyen, 1987). Of this, about 0.86 million tons were used in cement kilns and 0.37 tons were burned in cogeneration. All these sources were equipped with baghouses or electrostatic precipitators. No manganese emission factors for these exact sources were available. However, Pope (1987) reports emission factors of 29.4 and 47.3 picograms per joule of heat input for coal-fired industrial boilers equipped with multicyclones and scrubbers, respectively. According to the ARB, the average heating value of the coal burned in the state is 12,000 Btu/lb, or 2.53×10^{10} joules/ton. Low and high estimates of manganese emissions are thus:

$$\begin{aligned} \text{Low} &= (1.23 \times 10^6 \text{ tons})(2.53 \times 10^{10} \text{ J/ton})(2.94 \times 10^{-12} \text{ g/J})/(453.6 \text{ g/lb}) \\ &= 2.02 \times 10^3 \text{ lb} = 1.0 \text{ tons} \\ \text{High} &= (1.23 \times 10^6 \text{ tons})(2.53 \times 10^{10} \text{ J/ton})(47.3 \times 10^{-12} \text{ g/J})/(453.6 \text{ g/lb}) \\ &= 3.24 \times 10^3 \text{ lb} = 1.6 \text{ tons} \end{aligned}$$

19.3.2.2 Fuel Oil

The manganese content of residual fuel oil ranges from about 0.012 to 0.27 parts per million by weight (USEPA, 1984a). No Mn emission factors for residual oil combustion are available. An absolute upper bound estimate may be obtained, however, by assuming that all the manganese in the residual oil burned in California for electric power generation is emitted. In 1984, 2,061,800 bbl of fuel oil were consumed for this purpose in the state

(Barnett, 1986). Assuming a density of 7.88 lb/gal of fuel oil (USEPA, 1976), we can estimate maximum manganese emissions from electric power generation in the state as follows:

$$\begin{aligned}\text{Lower bound} &= (2,061,800 \text{ bbl})(42 \text{ gal/bbl})(7.88 \text{ lb/gal})(1.2 \times 10^{-8}) \\ &= 8 \text{ lb/yr} = 4 \times 10^{-3} \text{ ton/yr} \\ \text{Upper bound} &= (2,061,800 \text{ bbl})(42 \text{ gal/bbl})(7.88 \text{ lb/gal})(2.7 \times 10^{-7}) \\ &= 184 \text{ lb/yr} = 0.09 \text{ ton/yr}\end{aligned}$$

19.3.3 Emissions from Motor Vehicles

Manganese emissions from motor vehicle use may result from the presence of Mn in the gasoline and from the use of methylcyclopentadienyl manganese tricarbonyl (MMT) as a fuel additive. Emissions from use of manganese additive-free gasoline have been estimated by the ARB to be about 48 to 160 $\mu\text{g}/\text{mi}$ (Gentel et al., 1974a, 1974b). To obtain a rough estimate of the statewide emissions from this source, we assume that this range applies to all vehicle types. Total vehicle miles traveled in California in 1985 were 1.7×10^{11} (Avlani, 1986). Manganese emissions from automobiles and trucks would therefore be:

$$\begin{aligned}\text{Lower bound} &= (1.7 \times 10^{11} \text{ mi})(48 \times 10^{-6} \text{ g/mi})/(453.6 \text{ g/lb}) \\ &= 1.8 \times 10^4 \text{ lb/yr} = 9.0 \text{ tons/yr}\end{aligned}$$

$$\begin{aligned}\text{Upper bound} &= (1.7 \times 10^{11} \text{ mi})(160 \times 10^{-6} \text{ g/mi})/(453.6 \text{ g/lb}) \\ &= 6.0 \times 10^4 \text{ lb/yr} = 30 \text{ tons/yr}\end{aligned}$$

MMT was added as an octane booster to approximately 40 percent of unleaded gasoline until September 1978, when such use was banned by Section 211(f)(3) of the Clean Air Act, which prohibits use of fuel additives which "will cause or contribute to the failure of an emission control device or system ... to achieve compliance by the vehicle with ... emission standards." The EPA lifted the ban from May 31 to October 1, 1979 to compensate for a shortage of unleaded fuel (Anon., 1979a, 1979b). Refiners were allowed to add 1/32 g of MMT (as Mn) per gallon of unleaded gasoline. Automakers were

opposed to the lifting of the ban because of potential damage to catalytic converters, while the ARB expressed concern that the addition of MMT would result in increased hydrocarbon emissions (Anon., 1981). Ethyl Corporation, the primary manufacturer of MMT, requested a waiver of Section 211(f)(3) for addition of 1/64 g MMT per gallon of gasoline (Anon., 1981), but it was not granted. However, approximately 20 percent of leaded fuels still contain it at about 0.05 g Mn/gal (USEPA, 1984a).

Only a few studies of Mn emissions from use of MMT in fuels have been published. Ter Haar et al. (1975) found that 98.7 of the Mn emissions from MMT use are inorganic, and are mainly in the form of Mn_3O_4 . Any uncombusted MMT would likely photochemically decompose in a few seconds upon exposure to sunlight (Stober and Hertel, 1984). It also reacts rapidly with the hydroxyl radical. Manganese emission rates reported in the literature are generally based upon the assumption that all Mn present as MMT is emitted. Emission factors vary from 0.5 to 580 g/mi, depending upon assumptions as to MMT content and miles per gallon obtained by the vehicle (Stober and Hertel, 1984). Pierson et al. (1978) estimated emission rates of 50 to 80 $\mu\text{g}/\text{mi}$ during 1975-1976, when MMT use was about 1 - 4 mg Mn/gal. In 1977, when MMT use was about 16 mg Mn/gal, emissions were estimated to be about 130 $\mu\text{g}/\text{mi}$.

A very rough estimate of Mn emissions from use of MMT-containing leaded fuels in California may be obtained by assuming that 48 percent of the gasoline sold in California is leaded (Bloomhardt and Pelland, 1985), 20 percent of this fuel contains MMT, and the average automobile mileage is 17 miles per gallon (Stober and Hertel, 1984). A statewide emission factor would be:

$$\begin{aligned} \text{EF} &= (0.48)(0.2)(0.05 \text{ g Mn/gal})/(17 \text{ mi/gal}) \\ &= 282 \mu\text{g}/\text{mi} \end{aligned}$$

In 1985, the vehicles miles traveled by automobiles and light-duty trucks totalled about 1.49×10^{11} (Avlani, 1986). Ignoring mileage for medium duty trucks and heavy duty trucks, and assuming that all automobiles and light-duty trucks are gasoline-powered, results in an emission estimate of $(1.49 \times 10^{11} \text{ mi})(282 \times 10^{-6} \text{ g}/\text{mi})/(453.6 \text{ g}/\text{lb}) = 93,000 \text{ lb}$ or 46 tons per year.

The ARB recently surveyed vehicle and engine manufacturers to ascertain whether manganese-based compounds were being considered for use in meeting the California standard for particulate emissions from light-duty vehicles and/or the federal heavy-duty particulate emission standard (Drachand, 1985). Of the 15 respondents, 12 indicated that they were considering use of manganese, chiefly as a fuel additive. The purpose of the manganese is to lower the exhaust temperature necessary to regenerate particle traps (Wiedemann et al., 1983). The ARB estimates that by 1990, 2.6 - 6.6 percent of the vehicle fleet will have particle traps (CARB, 1984). This estimate was made during a period when gas prices were considerably higher than they are today, with further price increases forecast.

Volkswagen has proposed using Lubrizol 8220, a manganese-containing additive, to purge and regenerate ceramic particulate trap filters for diesel engines (Grumbly, 1985). The additive consists of non-stoichiometric Mn-fatty acid salts dissolved in solvent naphtha and contains 4.3 to 4.6 percent Mn (Wiedemann and Neumann, 1985). According to Stober and Hertel (1984), Lubrizol added to fuel at 0.3 g Mn/gal would produce emissions of 10 mg Mn/mi, assuming 30 mi/gal diesel fuel consumption. The exhaust gas emissions may be in the form of manganese oxides of all valence states, as well as $MnSO_4$ (Wiedemann and Neumann, 1985).

Volkswagen estimates that emission rates will range from an expected value of 1.38 mg Mn/mi to a worst case 4 mg Mn/mi (Wiedemann and Neumann, 1985). Street driving emission rates will vary from an expected value of 3.13 mg Mn/mi to a worst case 10 mg Mn/mi. The worst-case numbers are based on the assumption that all of the manganese in the fuel is emitted, while the expected values reflect realistic Mn retention in the engine and on the particle filter (Grumbly, 1985). These emission rates are 2 to 20 times larger than those previously estimated from use of MMT in unleaded gasoline.

19.3.4 Emissions from Crustal Materials and Soils

Manganese is widely distributed in the earth's crust, with an average concentration of approximately 1,000 ppm by weight and a range of nearly 0 to 7,000 ppm (USEPA, 1984a). Manganese concentrations in soils range 1 to 3,000

ppm, with one study reporting a mean of 560 ppm (USEPA, 1984a). Soil materials may be entrained into the atmosphere by a number of natural and anthropogenic processes, including suspension of road dusts, wind erosion, suspension of soils, and rock quarrying. The relative concentration of these sources has been modeled for several cities, but no data appear to exist on total manganese generated by each source.

19.4 INDUSTRIAL USE AND EMISSIONS

Manganese is an essential additive to iron and steel products. It increases the strength, toughness, hardness, and hardenability of steel, and inhibits formation of embrittling grain boundary carbides. These properties make manganese critical for the defense industry as well as for the proper functioning of much of domestic industry. Manganese is also an important constituent of several nonferrous alloy systems. Its principal nonferrous alloy use is in combination with aluminum to improve corrosion resistance. Aluminum alloys are widely used in beverage cans and in food-handling equipment. Copper-base alloys are used for marine propellers and fittings, gears, and bearings. Copper and copper-nickel alloys, which contain small amounts of manganese, are also used in electrical products such as thermostats and resistors (Jones, 1984, 1985).

A widespread, although minor, use of manganese is in battery oxide in the common "carbon-zinc" dry cell. Manganese dioxide is the form that is added to batteries. Miscellaneous other minor uses for manganese are (manganese sulfate and manganous oxide) soil conditioners; manufacture of welding-rod coatings and fluxes; coloring bricks and ceramics; and manganese-zinc ferrites for electronics. Table 19.4-1 shows estimated production capacities and uses for various manganese compounds. We believe that the manufacture of most of these products, other than iron or steel, does not take place in California.

In 1984, about 452,000 tons of steel were produced in California (Nash, 1986). The U.S. Environmental Protection Agency reports emission factors of 0.0008 to 0.026 lb of manganese per ton of steel produced in

Table 19.4-1
ESTIMATED UNITED STATES CAPACITY
AND USE OF SELECTED MANGANESE COMPOUNDS

Product	Formula	Estimated U.S. Capacity (MT/yr)	Use
Electrolytic manganese dioxide	MnO ₂	18,000	Dry-cell batteries; ferrites
High purity manganese oxide	MnO	9,000	High-quality ferrites; ceramics; intermediate for high purity Mn(II) salts
60 percent manganese oxide	MnO	36,000	Fertilizer; feed additive, intermediate for electrolytic manganese metal and dioxide
Manganese sulfate	MnSO ₄	68,000	Feed additive; fertilizer; intermediate for many products
Manganese chloride	MnCl ₂	3,000	Metallurgy; MMT synthesis; brick colorant; dye; dry-cell batteries
Potassium permanganate	KMnO ₄	14,000	Oxidant; catalyst; intermediate; water and air purifier
Methylcyclopentadienyl manganese tricarbonyl (MMT)	CH ₃ C ₅ H ₄ Mn(CO) ₃	500-1,000	Fuel additive

Source: USEPA (1984a).

furnaces (Pope, 1987). The low and high ends of the range correspond to use of fabric filters and electrostatic precipitators, respectively, to control emissions. Application of the emission factors to the California steel production rate results in the following emission estimates:

$$\begin{aligned} \text{Low estimate} &= (452,000 \text{ tons})(0.0008 \text{ lb/ton}) \\ &= 361 \text{ lb} = 0.18 \text{ tons} \end{aligned}$$

$$\begin{aligned} \text{High estimate} &= (452,000 \text{ tons})(0.026 \text{ lb/ton}) \\ &= 11,752 \text{ lb} = 5.9 \text{ tons} \end{aligned}$$

According to Penton Publishing (Gibson, 1986), there are 60 gray cast iron, 32 ductile cast iron, and 70 cast steel foundries in California. Information regarding the amounts of manganese used, or cast iron produced, by these foundries is not readily available. However we do know that the 1984 ratio of national cast iron manufactured to that of steel production was 0.031. As a rough approximation, we also assume that cast iron foundries in California produce 3.1 percent of the raw steel processed in the state. Cast iron production would therefore be about $(0.031)(452,000 \text{ tons}) = 14,000 \text{ tons}$. The EPA has published manganese emission factors of 0.003 to 0.075 lb per ton produced for cast iron production with a cupola furnace (Pope, 1987). If these apply to the majority of cast iron foundries in the state, then emissions would be:

$$\begin{aligned} \text{Low estimate} &= (14,000 \text{ tons})(0.003 \text{ lb/ton}) \\ &= 42 \text{ lb} = 0.02 \text{ ton} \end{aligned}$$

$$\begin{aligned} \text{High estimate} &= (14,000 \text{ tons})(0.075 \text{ lb/ton}) \\ &= 1,050 \text{ lb} = 0.52 \text{ ton} \end{aligned}$$

A recent survey by the Bay Area Air Quality Management District (Hill, 1985) identified 40 firms which use manganese compounds. These are listed in Table 19.4-2. Emission estimates were not available for any of the facilities.

Table 19.4-2
MANGANESE EMISSIONS IN THE SAN FRANCISCO BAY AREA

Source	City	Emissions (tons/yr)
<u>Alameda</u>		
Berkeley Forge & Tool Inc.	Berkeley	T
Cal/Ink Division	Berkeley	T
DOE-Sandia National Laboratory	Livermore	T
Jones-Hamilton Company	Newark	U
Kaiser Aluminum & Chemical	Pleasanton	T
Kraftile Company	Fremont	T
Lawrence Livermore National Laboratory	Livermore	T
Macaulay Foundry, Inc.	Berkeley	T
Naval Air Station Alameda	Alameda	T
Northwestern Venetian Supply	Oakland	T
Pacific Steel Casting Co.	Berkeley	T
Peterbilt Motors Co.	Newark	T
Transamerica Delaval Inc.	Oakland	T
Vulcan Steel Foundry Company	Oakland	T
<u>Contra Costa</u>		
California & Hawaiian Sugar	Crockett	T
Central Contra Costa Sanitation District	Martinez	T
Chevron Research Company	Richmond	T
Crown Zellerbach Corp.	Antioch	U
Delta Diablo Sanitation	Antioch	T
Great Western Chemical Co.	Richmond	T
Landsea Oil Company	Martinez	T
Radiant Color	Richmond	T
US Steel Corp.	Pittsburg	T
West Contra Costa Sanitation District	Richmond	T
<u>Marin</u>		
Central Marin Sanitation District	San Rafael	T
<u>San Francisco</u>		
Glidden Coatings & Resin	San Francisco	T
L & H Paint Products	San Francisco	U
Louis Roesch Company	San Francisco	T
<u>San Mateo</u>		
Ampex Corporation	South San Francisco	T
Fuller-O'Brien Div.	South San Francisco	T

Table 19.4-2 (Continued)

Source	City	Emissions (tons/yr)
GTE Products Corporation	Belmont	T
O K Radiator	Redwood City	T
<u>Santa Clara</u>		
Bay City Foundry Co.	Santa Clara	T
General Electric Co.	San Jose	T
Hewlett-Packard Co.	Palo Alto	T
Lockheed Missiles & Space	Sunnyvale	U
Syntex (USA) Inc.	Palo Alto	T
Varian Associates	Palo Alto	T
<u>Sonoma</u>		
Cal-Wood Door	Rohnert Park	T
Hewlett-Packard Company	Santa Rosa	T

Source: Bay Area Air Quality Management District (Hill, 1985).

^aT = 0-0.1 tons/yr; U = Manganese is handled but emissions cannot be estimated from available information.

19.5 CONSUMER USE AND EMISSIONS

Although a substantial amount of manganese is present in many consumer products such as those which use aluminum, steel, cast iron, and copper, it is present in the form of an alloy and does not contribute to air emissions. Non-alloy consumer uses for manganese are manganese dioxide in batteries, and manganese sulfate and manganous oxide in soil conditioners. Some manganese sulfate and manganous oxide might become suspended in air at the time of soil application, or might be entrained as the soil dries. Neither the extent of use of manganese as a soil conditioner in California, nor soil conditioner emission factors are known.

19.6 EMISSION SUMMARY

Manganese is not produced in California. Indirect emission sources in the state include natural sources such as soil, road dust, and burning vegetation; and anthropogenic sources such as auto exhaust, combustion of residual oil and coal, glass furnaces, paper and pulp process combustion, asphalt production, and sewage sludge incineration. The following estimates of manganese emitted by indirect sources may have large uncertainties because of the uncertainty in some of the parameters used in the calculations.

A rough estimate of manganese emissions from sludge incineration is 3 to 18 lb/yr. Coal combustion contributes 1.0 to 1.6 tons per year. Between 8 and 184 lb Mn/yr are emitted by the combustion of residual fuel oil in the state. Between 9 and 30 tons Mn/yr are estimated to be emitted by automotive exhaust, due to the presence of manganese in the gasoline. MMT, added as an octane booster, contributes another 46 tons of manganese from automotive exhaust. Manganese is being considered as an additive to diesel fuels to help purge and regenerate ceramic particulate trap filters in diesel engines.

The primary alloy use of manganese is as an additive to strengthen and harden iron and steel products, although minor uses exist in copper, nickel, and aluminum alloys and in battery oxide in the carbon-zinc dry cell battery. We estimate that emissions from steel production are 0.18-5.9 tons/yr and those from cast iron production are about 0.02 to 0.52 ton/yr.

Manganese sulfate and manganous oxide are used in soil conditioners. The extent of production of airborne manganese from this source is not known. Total statewide emissions accounted for in this review are about 56 to 84 tons per year.

19.7 ATMOSPHERIC CONCENTRATIONS

According to a recent analysis of historical data by the U.S. Environmental Protection Agency (USEPA, 1984a), ambient particulate manganese concentrations in urban areas of the U.S. have decreased over the past 30 years. Between 1970 and 1982, for example, the geometric mean concentration for urban sites in the EPA's National Air Surveillance Networks (NASN) declined from 0.04 to 0.024 $\mu\text{g}/\text{m}^3$.

Relatively few data are available on atmospheric manganese concentrations in California. Table 19.7-1 shows annual averages of quarterly composite manganese concentrations measured at 19 California NASN stations in 1970-1974. Entries marked "ND" correspond to years in which data were considered by the EPA to be invalid for at least one quarter. For all of the cities, annual average manganese concentrations declined over the five years. More recently, the California Aerosol Characterization Experiment (ACHEX) measured manganese concentrations of 0.030 to 0.096 $\mu\text{g}/\text{m}^3$ in West Covina, Pomona, Rubidoux and Dominguez Hills (Appel et al., 1980).

19.8 ATMOSPHERIC CHEMISTRY

The following is summarized from a recent review of the atmospheric chemistry of manganese by EPA (USEPA, 1984a). The most common manganese compounds in the coarse particulate of crustal origin are oxides and hydroxides, of oxidation states +2, +3 and +4, and manganese carbonate. Manganese emitted by metallurgical processes is normally in the form of oxides, and is present in highly enriched fine particles. Very little information on the atmospheric reactions of manganese is available. Manganese dioxide can react with SO_2 or NO_2 to form manganous sulfate (MnSO_4) and dithionate (MnS_2O_6) or manganese nitrate [$\text{Mn}(\text{NO}_3)_2$], respectively. Aerosols

Table 19.7-1
 CALIFORNIA MANGANESE CONCENTRATIONS MEASURED BY THE
 NATIONAL AIR SURVEILLANCE NETWORK

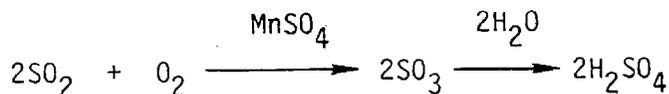
(Concentrations in $\mu\text{g}/\text{m}^3$)

Average of 4 Quarterly Composites					
	1970	1971	1972	1973	1974
Anaheim	0.035	0.039	0.020	ND	0.020
Berkeley	ND ^a	ND	0.009	0.012	0.007
Burbank	0.040	0.041	0.020	0.033	0.016
Fresno	0.035	ND	0.021	0.034	0.026
Glendale	0.026	0.024	0.017	0.015	ND
Long Beach	0.034	0.029	0.023	ND	0.033
Los Angeles	0.049	0.046	0.030	ND	0.024
Oakland	0.037	0.031	0.012	ND	0.021
Ontario	0.053	0.062	0.035	ND	ND
Pasadena (Site 1)	ND	0.029	ND	ND	ND
Pasadena (Site 2)	0.035	ND	ND	ND	0.020
Riverside	0.034	ND	ND	ND	ND
Sacramento	0.025	0.023	0.010	0.021	0.016
San Bernardino	0.066	0.053	0.047	ND	0.037
San Diego	0.022	ND	0.015	0.040	0.021
San Francisco	0.010	0.013	0.009	0.011	0.004
San Jose	ND	ND	ND	ND	0.016
Santa Ana	0.031	0.051	0.020	0.015	0.014
Torrance	0.029	ND	ND	0.022	0.020
Statewide Mean	0.035	0.037	0.020	0.022	0.020
Statewide Std. Dev.	0.013	0.014	0.011	0.011	0.009

Source: Data from National Air Surveillance Networks (Oakland, 1976).

^aData unavailable for all four quarters.

of manganous sulfate can catalyze the oxidation of atmospheric SO₂ to sulfur trioxide, thus promoting the formation of sulfuric acid:



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20.0
EVALUATION OF METHYL BROMIDE

20.1 PHYSICAL AND CHEMICAL PROPERTIES

Methyl bromide is a colorless gas at temperatures above 3.5°C. Table 20.1-1 summarizes some of its physical and chemical properties.

20.2 DIRECT PRODUCTION IN CALIFORNIA

20.2.1 Natural Sources

According to Singh (1984), strong evidence exists that oceans are a major source of methyl bromide. Surface seawater concentrations over the Eastern Pacific are 1.2 ± 0.8 ng/L. Using a two-film model, Singh computed the methyl bromide flux over the same area and extrapolated it to global waters. The rough approximation derived from this model suggests an oceanic source of 3×10^{11} g/yr (3.3×10^5 tons/yr). Neither the mechanism for production of methyl bromide in the marine environment nor is its oceanic distribution is well understood.

20.2.2 Anthropogenic Sources

In order to ascertain whether methyl bromide is manufactured in California, we called four companies which manufacture the chemical in the U.S.: Great Lakes Chemical Corporation, Ameribrom, Inc., Plainview Chemical Corporation, and Ethyl Chemicals Group (Farner, 1986; Kastens, 1986; Paren, 1986). None of these companies manufactures the compound in California. Furthermore, none of the company spokesmen knew of any California production; two of the representatives were fairly confident that the compound was not produced in California. A representative of Kerr-McGee Chemical Corporation stated that his firm does not produce methyl bromide in the State (Garrett, 1986).

Table 20.1-1
CHEMICAL DATA FOR METHYL BROMIDE

Property	Value for Methyl Bromide
CAS Registry No.	74-83-9
Synonyms	bromomethane
Molecular Weight	94.95
Molecular Formula	CH ₃ Br
Molecular Structure	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{Br} \\ \\ \text{H} \end{array}$
Physical State at STP	Colorless liquid or gas
Boiling Point	4.6°C
Melting Point	-93°C
Specific Gravity	1.736 @ -10°C
Vapor Pressure	2 atm @ 23.3°C
Vapor Density	3.27
Solubility	0.900 mg/L @ 20°C
Log Partition Coefficient (octanol/H ₂ O)	
Henry's Law Constant	

Source: Verschueren (1977); USDHHS (1984).

20.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

As discussed in Section 20.8, methyl bromide does not form in the atmosphere. To the best of our knowledge, there is also no other indirect production mechanism for methyl bromide in California.

20.4 INDUSTRIAL USE AND EMISSIONS

Methyl bromide's main use in California is as a soil fumigant. As seen in Table 20.4-1, 6,978,109 pounds of methyl bromide were applied for structural pest control in agriculture in California in 1984 (California Department of Food and Agriculture, 1985). In order to estimate emissions from agricultural applications, we used the ARB's method for area source emission category 47092, Agricultural Crops-Pesticide Application-Evaporation-Synthetic Pesticides (Ipps, 1982). For this preliminary analysis, we used annual activity code 23 and monthly meteorological data for Fresno County, as presented by Leung et al. (1980). According to our analysis, essentially all of the CH_3Br applied would ultimately be released to the atmosphere. Agricultural emission would therefore be about 3500 tons (3200 MT) per year.

Methyl bromide is also used industrially as a fumigant, disinfectant, methylating agent, and wool degreaser (USDHHS, 1984). It is presently not known to what extent these activities take place in California. As seen in Table 20.4-2, however, toxic air pollutant surveys by the South Coast Air Quality Management District (Zwiacher et al., 1983) and the Bay Area Air Quality Management District (Hill, 1985) identified several actual and potential sources. Statewide emissions from these sources are about 22 tons (20 MT) per year. Four listed companies, Niklor Chemical Company Inc. (Long Beach), Del Monte Corporation (San Jose), Stapleton Spence Packing (San Jose), and See's Candy Shops Inc. (Los Angeles), account for about 99 percent of the estimated industrial emissions. The largest emitter, Niklor Chemical Company, formulates a methyl bromide-containing pesticide (Wilhelm, 1986). The other three significant emitters appear to use the compound as a disinfectant or fumigant. Information on how the two districts' estimates were obtained was unavailable.

Table 20.4-1
METHYL BROMIDE APPLICATION DURING 1984

Commodity	Pounds Applied	Commodity	Pounds Applied
Alfalfa	55.18	Open Land	83,217.23
Almonds	112,591.87	Orange	5,826.66
Apple	72,681.69	Orchard Floors	16,871.33
Apricot	5,001.50	Ornamentals	150,095.62
Avocado	3,319.26	Pasture/Rangeland	196.00
Barley	182.22	Peach	81,262.38
Beans	8,487.58	Pear	1,300.00
Beets	7.84	Peas	158.21
Berries, other	8,561.54	Peppers (Bell)	36,733.02
Brussels Sprouts	18,177.62	Peppers (Chili)	1,930.62
Buildings	250.00	Pistachio	9,563.47
Bulbs	3,571.51	Plum	1,921.78
Carrot	3.92	Pomegranate	526.50
Cherries	10,297.91	Potato	5.88
Citrus	7,095.16	Prune	40,852.71
Landscape Maintenance	69,175.90	Public Health Pest Control	450.00
Conifers	15,001.28	Quince	33.32
Corn	1,330.9	Radish	3.92
Cucumber	13.95	Regulatory Pest Control	6.24
Date	6,119.02	Residential Areas	758.25
Deciduous Ornamental Trees	131,296.35	Rice	5,202.85
Dried Fruit	167,697.11	Rights of Way	904.13
Evergreen Trees	7,470.50	Roses	247,366.40
Fallow Farm Land	108,968.55	Shrubs	2,154.00
Figs	283.07	Soil Fumigation	232,622.79
Flowers	231,444.26	Spices	58.40
Food Processing Plants	2.50	Spinach	3.92
Forest/Timberland	399.81	Squash	3.92
Garlic	39.20	Storage Buildings, Other	8,969.35
Grain	190.50	Strawberries	1,924,254.07
Granary	521.47	Structural Control	2,991.17
Grapes	972,619.89	Structural Pest Control	1,489,504.46
Grapefruit	31,753.30	Sunflower	9.80
Greenhouse Fumigation	710.19	SweetPotato	7,245.78
Household	21.60	Tomato	44,905.25
Industrial Areas	6,604.03	Tropical and Sub-Tropical Fruits	2,765.11
Kiwi	16,142.99	Turf	381,252.36
Lemon	3,573.78	Vegetable Seed	124.46
Lettuce (Head)	428.34	Vertebrate Pest Control	19.90
Melons	2.94	Walnut	103,105.06
Miscellaneous	9,561.11	Water Areas	9.80
Nectarines	12,816.67	Watermelons	3.92
Non-Agricultural Areas	6,146.98	Wheat	2,111.43
Nuts, Other	110.91		
Oats	36.00		
Okra	7.98		
Onions	40,031.84		

Source: State of California, Department of Food and Agriculture, Annual Pesticide Use Report by Chemical, January through December, 1984.

Table 20.4-2
 REPORTED METHYL BROMIDE EMITTERS IN CALIFORNIA

	City	County	Emission Estimate	
			SCAQMD lb/yr	BAAQMD kg/yr
Conagra, Inc.	Oakland	Alameda		400
Del Monte Corporation #5	San Jose	Santa Clara		180
DOE-Sandia National Laboratory	Livermore	Alameda		4,800
Dysan Corporation	Santa Clara	Santa Clara		T ^a
Fairchild Camera and Instruments	San Jose	Santa Clara		T
Henry E. Huntington Library & Art	San Marino	Los Angeles	50	22.7
Jones-Hamilton Company	Newark	Alameda		U ^a
Lawrence Livermore National Lab.	Livermore	Alameda		T
Los Angeles County Sanitation Dist.	Carson	Los Angeles	1	.5
Niklor Chemical Company Inc.	Long Beach	Los Angeles	34,000	15,419.5
See's Candy Shops Inc.	Los Angeles	Los Angeles	792	359.2
Soundcast Company	Costa Mesa	Orange	1	.5
Southwest Plating Company	Los Angeles	Los Angeles	1	.5
Spencer Electro Plating Company	Burbank	Los Angeles	12	5.4
Sphinx Manufacturing Company	Los Angeles	Los Angeles	2	.9
Stapleton Spence Packing	San Jose	Santa Clara		
Stewart-Filmscreen Corp.	Torrance	Los Angeles	5	2.3
The Stroh Brewery Company	Van Nuys	Los Angeles	1	.5
Superchrome Plating & Engr. Co.	Los Angeles	Los Angeles	1	.5
Van Waters & Rogers	San Jose	Santa Clara		T
				3,200
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20.5 CONSUMER USE AND EMISSIONS

Potential routes for consumer exposure would be the use of methyl bromide in special purpose fire extinguishers and consumption via the residue left on food crops due to inadequate removal. Methyl bromide may comprise up to 100 percent of the chemical make-up of fire extinguishers (Sittig 1981).

20.6 EMISSION SUMMARY

Methyl bromide is not manufactured in California. Potentially large amounts of the compound may be produced in the ocean off the California coast, although this remains unconfirmed at present. No indirect production of methyl bromide takes place in the state. It is not known to what extent industrial processes use the chemical as a methylating or wool degreasing agent or disinfectant. However, processes which use these compounds are likely to use only minor amounts compared to agricultural activities. About 3,500 tons/year (3,200 MT/yr) of methyl bromide are released through use of the compound as a soil fumigant for a variety of crops in California. Methyl bromide may also be released through its use in special purpose fire extinguishers.

20.7 SUMMARY OF AMBIENT CONCENTRATION DATA

There is a substantial body of information regarding ambient levels of methyl bromide. This information is compiled in Table 20.7-1 for all measurements carried out in California. Measurements performed outside of California are also included for comparison.

The data compiled by Brodzinsky and Singh (1983) from earlier work of Singh and coworkers (e.g. Singh et al., 1981) indicate mean urban values of 30-250 ppt with maxima of 100-900 ppt. Annual averages (year 1980) of Guicherit and Schulting (1985) for three sites in the Netherlands are consistent with these values. "Background" methyl bromide concentrations at remote continental sites are about 5 ppt. Higher values are recorded at coastal locations and may reflect oceanic sources, transport of urban CH_3Br , or both.

Table 20.7-1
 MEASURED AMBIENT CONCENTRATIONS OF METHYL BROMIDE
 (Concentrations in ppt)

Location	Concentration		Reference
	mean	max.	
Los Angeles, CA	244	894	Singh et al., 1981
Oakland, CA	55	108	
Phoenix, AZ	67	190	
Badger Pass, CA	4.8	8.0	Brodzinsky and Singh, 1983
Denver, CO	120	190	
Houston, TX	100	170	
Jetmore, KS	5.0	5.0	
Los Angeles, CA ^a	150	580	
Menlo Park, CA	16	16	
Mill Valley, CA	25	25	
Oakland, CA ^a	55	78	
Palm Springs, CA	24	24	
Phoenix, AZ ^a	67	120	
Point Arena, CA	17	20	
Point Reyes, CA	93	93	
Reese River, NV	5.0	5.0	
Riverside, CA	250	560	
San Jose, CA	31	31	
St. Louis, MO	81	100	
Delft, Vlaardingen and Terschelling, The Netherlands ^b	50-200	100-900	Guicherit and Schulting, 1985
Dominguez Hills, CA	ND ^c	-	Shikiya et al., 1984 ^d
Riverside, CA	ND	-	
Los Angeles, CA	ND	-	
El Monte, CA	450	1,300 ^e	
Dominguez Hills, CA	ND	-	Air Resources Board ^f
Riverside, CA	ND	-	
Los Angeles, CA	ND	-	
El Monte, CA	ND	-	

^aIncludes substantial overlap with data reported in Singh et al. (1981).

^bAbout 350 samples per site during 1980.

^cND = none detected with a detection limit of 200 ppt.

^dStudy period: November 1982-December 1983.

^eOnly 8 percent of the values were above the detection limit of 200 ppt.

^fStudy period: January-August 1984 (McNerny, 1985).

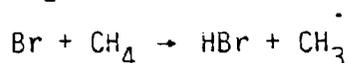
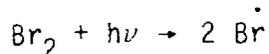
Shikiya et al. (1984) collected 24 hour-integrated samples at four sites in the South Coast Air Basin: downtown Los Angeles, El Monte, Dominguez Hills, and Riverside. Samples were collected every 2 to 5 days, yielding about 6 to 20 data points per month per site. The stated detection limit for methyl bromide was 200 ppt, which is higher than most mean values reported by Brodzinsky and Singh (1983) and Guicherit and Schulting (1985). With this high detection limit, methyl bromide was not detected at three of the four sites, and was detected in only 8 percent of the samples at the remaining site, El Monte. During November 1982 - December 1983 the maximum value, highest monthly mean and composite mean at the El Monte site were 1,300 ppt, 560 ppt and 450 ppt, respectively. A strong seasonal variation was observed, with winter maxima of 360-560 ppt (monthly averages) and summer minima of less than 200 ppt (the detection limit). These values appear consistent with those reported in earlier studies of methyl bromide in urban air.

The monitoring study initiated by the Air Resources Board in November 1982 is an on-going effort expected to last several years. The initial results reported by Shikiya et al. (1984) covered November 1982 - December 1983. Data printouts covering January 1984 - August 1984 have been made available to us by the ARB (McNerny, 1985): During this period, and with the same detection limit of 200 ppt, no methyl bromide was recorded at the Dominguez Hills (27 samples), Riverside (32 samples), Los Angeles (31 samples) or El Monte sites (135 samples).

20.8 ATMOSPHERIC CHEMISTRY

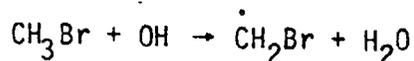
20.8.1 In-Situ Formation

There are no reactions by which methyl bromide may form in the atmosphere. The reaction of bromine atoms with methane does not involve substitution to yield CH_3Br but proceeds by H-atom abstraction to form hydrogen bromide and methyl radicals:



20.8.2 Removal Processes

Methyl bromide is one of the least reactive Level 2 compounds, with a correspondingly long persistence in the atmosphere. Reactions with O_3 and NO_3 are negligibly slow. Photolysis is a negligible removal process for CH_3Br in the lower troposphere (Robbins, 1976). Methyl bromide reacts only slowly with the hydroxyl radical:



with a reaction rate constant of $3.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. This corresponds to a half life of 5 to 11 months. Upward diffusion and deposition are thus the dominant loss processes for CH_3Br in the troposphere.

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. 21.0
EVALUATION OF MERCURY

21.1 PHYSICAL AND CHEMICAL PROPERTIES

Although several forms of organic and inorganic mercury are used in California, this evaluation was limited to elemental mercury, which is a silvery mobile liquid. Table 21.1-1 summarizes some of its physical and chemical properties.

21.2 DIRECT PRODUCTION IN CALIFORNIA

21.2.1 Natural Sources

Natural evaporation or "outgassing" of mercury vapor from rocks, soils, and the oceans probably accounts for most of the loading of mercury into the atmosphere (Van Horn, 1975; Wollast et al., 1975), although the magnitude of these sources in California has not been estimated. In addition, both aerobic and anaerobic bacteria in aqueous sediments can reduce mercuric (Hg^{2+}) mercury to elemental mercury, which can eventually volatilize (Holm and Cox, 1974; Wood, 1974).

21.2.2 Anthropogenic Sources

The number of mercury producing mines in the U.S. has fallen from a high of 197 in 1941 to only 3 in 1984. Of these three mines, only one produced mercury as a primary product; the others produced mercury as a byproduct of gold mining. In 1984, U.S. production was 19,048 flasks (1 flask equals 76 pounds), down from 25,070 flasks in 1983. This decrease can be attributed to a large increase in mercury imports from 1983 to 1984. Secondary production, which includes mercury recovered from old batteries, electronic equipment, dental amalgams, industrial and municipal sludges, and metal recovered from chlorine and caustic soda plants, amounted to 5,217 flasks during 1984.

U.S. mining production of mercury in 1984 comprised 24 percent of

Table 21.1-1
CHEMICAL DATA FOR ELEMENTAL MERCURY

Property	Value for Elemental Mercury
CAS Registry No.	7439-97-6
Synonyms	Quicksilver
Molecular Weight	200.6
Molecular Formula	Hg
Molecular Structure	Hg ⁰
Physical State at STP	Silver liquid
Boiling Point	357°C
Melting Point ^a	-38.87°C
Specific Gravity ^a	13.55 @ 20°C
Vapor Pressure ^b	0.001201 mm @ 20°C 0.002777 mm @ 30°C
Vapor Density (air=1)	6.90
Solubility	
Log Partition Coefficient (Octanol/H ₂ O)	
Henry's Law Constant	

Source: Burrows et al. (1974), unless otherwise noted.

^aWeast and Astle (1981).

^bNIOSH (1973).

domestic supply. Government shipments from the national defense stockpile accounted for 5 percent, secondary production for 6 percent, industry stocks for 33 percent, and imports for 31 percent (USD0I, 1985a; 1985b).

Although there used to be significant mining for mercury ore in California, that is no longer the case. The Lake County Air Pollution Control District has identified one small mine in Napa and Yolo Counties that still produces some mercury, in conjunction with its primary purpose, mining for gold (Kauper, 1986). This mine produces approximately 40 to 50 flasks of mercury per year (Carillo, 1985). The ore processing facilities for the mine are in Lake County. Emission sources include the mill, oxidation autoclave, electrowinning process, heated filter in a kiln and an induction furnace. The Lake County APCD estimates emissions of about 4.5 lb/week, or 0.12 ton/yr (Kauper, 1986). A few other small gold mines may produce some mercury, but, since mining companies are not required to report production, their output is unknown. However, it is likely that such production will be quite small, if it exists (Carillo, 1985).

21.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

Mercury may be emitted through combustion or use of materials of which it is an ingredient. In California, these materials include solid waste and sludge, geothermal steam, and residual fuel oil.

21.3.1 Solid Waste and Sludge Incineration

A recent review of several sludge studies covering 268 publicly-owned treatment works (Fricke and Clarkson, 1984) found that mercury was present in all of the samples collected. The quality of the data varied widely, in that samples were taken from different points in the waste treatment process in different plants, and various analytical methods were used. Mercury concentrations in sludge varied from 0.01 to 130 mg/kg dry weight, with a weighted mean (weighted by number of treatment plants) of 4.3 mg/kg. These results may be compared with those presented by Gerstle and Albrinck (1982), who found the concentration of mercury in municipal sewage sludges to range from 0.1 to 89 mg/kg dry weight, with a mean and median of 7 and 4 mg/kg,

respectively. Since mercury's boiling point (350°C at 1013 kPa) is lower than the temperatures reached in conventional incineration equipment (760 to 815°C), virtually all of the incoming mercury is expected to volatilize (Gerstle and Albrinck, 1982).

Although the foregoing indicates a strong potential for mercury emissions from municipal sludge incineration, no measurement data on emissions are available. Radian Corporation (1985) reviewed most or all of the sewage sludge incinerator source test data maintained by the U.S. Environmental Protection Agency (EPA) and found no data for mercury. It is not clear whether mercury was undetected or no attempt was made to identify and/or quantify it. Examination by SAIC of one set of sludge incinerator tests (Bennett et al., 1984) indicates a low potential for detecting mercury even if had been present. Particulate samples were collected on heated filters. Since most of the elemental mercury present in the incinerator emissions would likely be in the form of mercury vapor, it probably passed through the sampling train uncollected.

According to the ARB (Woodhouse, 1987), sludge is currently incinerated at seven wastewater treatment plants in California. Table 21.3-1 lists these plants, along with their estimated incineration rates. About 17,000 dry tons of sludge are burned annually. Using Fricke and Clarkson's weighted mean of 4.3 mg Hg per dry Kg of sludge, we estimate the potential for about 0.07 ton/yr of mercury emissions from this source.

In a recent review of EPA data, Bloomhardt and Pelland (1985) identified 10 municipal incinerators in California which may be sources of mercury emissions. Emissions data on these facilities were, however, unavailable.

21.3.2 Geothermal Emissions

Power plants and other facilities which use geothermal steam in California are potential sources of mercury emissions. Geothermal fluid is now being used for electrical generation in California in the four-county

Table 21.3-1
MERCURY EMISSIONS FROM SLUDGE COMBUSTION IN CALIFORNIA

Facility	County	Dry Sludge Burned (tons/yr)	Mercury Emissions (lb/yr)
Doc May Regional WWTP	Santa Clara	876	8
City of San Mateo WQCP	San Mateo	2,081	18
Central Contra Costa Sanitary Dist.	Contra Costa	12,410	107
South Tahoe Public Utility District	El Dorado	37 ^a	0
Yosemite National Park	Mariposa	84	1
City of San Clemente	Orange	1,219	10
Barstow Wastewater Reclamation Facility	San Bernardino	424	4
Total for California		17,131	147

^aMean of low and high burn rates.

Geysers-Calistoga Known Geothermal Resources Area, which is about 70 miles north of San Francisco. Under normal operating conditions, geothermal steam is directed through a turbine and then into a direct-contact condenser. The hot condensate is pumped to a cooling tower and the noncondensable gases are removed from the condenser and then injected into cooling towers. High-temperature, high-pressure steam from the geothermal reservoir at The Geysers travels to wells through fractures in Franciscan graywacke, a type of sandstone (Rogozen et al., 1981). Through contact with the rock, the steam picks up a variety of particulate compounds and entrains elemental mercury. Tests conducted by Battelle Pacific Northwest Laboratory (Robertson et al., 1977) on five wells at The Geysers detected from 1,800 to 5,800 $\mu\text{g}/\text{m}^3$ of mercury in the incoming steam; of this, 72 to 79 percent was in the form of elemental mercury vapor. These same researchers found 0.18 to 0.59 $\mu\text{g}/\text{m}^3$ of mercury in the exhaust from five of the Pacific Gas and Electric Company (PG&E) geothermal power plant cooling towers at The Geysers. (Higher values were measured but they are believed by Robertson et al. to be due to contamination of sampling and analytical equipment.) In the one tower for which a partitioning of mercury species was determined, Hg^0 constituted 84 - 87 percent of the total. In a later study, Robertson et al. (1981) measured 0.16 to 1.13 $\mu\text{g}/\text{m}^3$ in the exhaust of the cooling tower associated with PG&E's Unit 15. Subsequent emissions tests on this tower by SAIC (Rogozen et al., 1981) found 1.0 to 1.2 $\mu\text{g}/\text{m}^3$.

Robertson et al. (1977) estimated that mercury emission rates for 13 of the towers at The Geysers ranged from 0.63 to 1.6 g per megawatt electric (MWe) per day. The installed capacity of The Geysers at that time was 510 MWe (Rogozen et al., 1981). Thus, if elemental emissions constituted 84 to 87 percent of the total, then Hg^0 emissions from these towers were about 0.11 to 0.20 ton/yr. To this we must add an estimate of 0.11 to 0.14 ton/yr for the Unit 15 cooling tower (Rogozen et al., 1981). Finally, on the basis of tests conducted in 1984 at another geothermal power plant in the Geysers-Calistoga KGRA, SAIC estimates an additional 0.07 tons/yr of mercury emissions. Total emissions in the area, according to the Battelle and SAIC estimates, would be about 0.3 to 0.4 ton/yr of elemental mercury.

To update these estimates, we contacted the Northern Sonoma County and Lake County air pollution control districts, which confirmed that only minor amounts of mercury are released from steam at the Geysers geothermal power plants where emissions tests have been conducted (Tolmasoff, 1986; Reynolds, 1986). However, no systematic study of mercury in the vapor plumes of all 20 power plants currently operating in the Geysers-Calistoga KGRA has been conducted. On the basis of recent source tests, the Northern Sonoma County APCD estimated emissions of 0.00017 ton/yr from one plant (Tolmasoff, 1986).

21.3.3 Fossil Fuel Combustion

The U.S. Environmental Protection Agency, in a recent review of national standards for mercury emissions, discounted fossil fuel combustion as a significant mercury source, since expected ambient concentrations around power plants were not expected to exceed recommended levels (USEPA, 1984b). Nevertheless, we believed it important to confirm this judgment for California.

Mercury is present at about 60 to 690 parts per billion in western coals (Magee et al., 1973). According to the ARB, 1.23 million tons of coal were burned in California in 1985 (Nguyen, 1987). Of this, about 0.86 million tons were used in cement kilns and 0.37 tons were burned in cogeneration. Assuming that 90 percent of the mercury present in the coal is released (Rogozen and Hausknecht, 1978), maximum statewide emissions would be 0.066 to 0.76 tons/year.

A survey by Oglesby (1975) reported a range of 0.002 to 0.4 ppm of mercury in residual fuel oil, which comprises over 95 percent of the petroleum burned for electric power generation in the U.S. In 1984, 2,061,800 bbl of fuel oil were consumed in California for electric power generation (Barnett, 1986). Assuming a density of 7.88 lb/gal of fuel oil (USEPA, 1976), we can estimate mercury emissions from electric power generation in the state as follows:

$$\begin{aligned}\text{Lower bound} &= (2,061,800 \text{ bbl})(42 \text{ gal/bbl})(7.88 \text{ lb/gal})(2 \times 10^{-9}) \\ &= 1.4 \text{ lb/yr} = 7 \times 10^{-4} \text{ ton/yr}\end{aligned}$$

$$\begin{aligned}\text{Upper bound} &= (2,061,800 \text{ bbl})(42 \text{ gal/bbl})(7.88 \text{ lb/gal})(4 \times 10^{-7}) \\ &= 270 \text{ lb/yr} = 0.14 \text{ ton/yr}\end{aligned}$$

Thus mercury emissions from fossil fuel combustion are about the same order of magnitude as those from geothermal power production.

21.4 INDUSTRIAL USE AND EMISSIONS

Prior to World War II, the principal use of mercury in the United States was in the amalgamation process for the recovery of gold from its ores (USDOl, 1985b). The mercury amalgamation process is now used by only a few small mines (Carillo, 1985). However, the mercury-cell process for producing chlorine and caustic soda has become widespread in this country. In the 1970s, when the harmful environmental effects of mercury became better understood, the use of this process decreased considerably. By 1983 the chlor-alkali process accounted for only 16 percent of domestic consumption of mercury (USDOl, 1985b). No chlor-alkali processing plants presently exist in California (Carrico, 1986). Table 21.4-1 shows U.S. mercury consumption by use.

Our review of emission inventory data, prepared by the U.S. Bureau of Mines (Carrico, 1986), the South Coast Air Quality Management District (SCAQMD), and the Bay Area Air Quality Management District (BAAQMD), identified several industrial uses in California; these include recovery from electronic scrap and precious metals, component of certain electronic instrumentation, use in electroplating, fungicide component of paint (phenyl mercuric acetate), and used battery reclamation. Table 21.4-2 lists the mercury-using facilities identified by the Bureau of Mines and the two air quality management districts. About 0.24 ton of mercury is estimated to be emitted in the South Coast Air Basin, while the amount in the San Francisco area is unknown. In addition to the facilities listed in Table 21.4-2, we have identified one active mercury retorting facility, Quicksilver Products, Inc. in Brisbane. This plant reprocesses mercury through a vacuum filtration still and uses activated carbon to remove mercury vapors; according to the plant, its mercury emissions are negligible (Vaughn, 1986). Finally, Martin Metals, Inc. in Los Angeles reprocesses mercury but does not allow it to come into contact with air; thus no emissions occur (Troup, 1986).

Table 21.4-1

U.S. MERCURY CONSUMPTION, BY USE, 1980-1984

SIC code	Use	1980	1981	1982	1983	1984
28	Chemical and allied products:					
2812	Chlorine and caustic soda manufacture	9,470	7,323	6,243	8,054	7,347
2816	Pigments	W	W	W	W	W
2819	Catalysts, miscellaneous	765	815	499	484	359
2821	Catalysts for plastics	W	W	W	W	W
2819	Laboratory uses	363	328	281	280	217
2851	Paints	8,621	7,049	6,794	6,047	4,651
2879	Agricultural chemicals	W	79	36	W	W
36	Other chemicals and allied products	W	W	W	W	W
36	Electrical and electronic uses:					
3641	Electric lighting	1,036	1,043	826	1,273	1,487
3643	Wiring devices and switches	3,062	2,641	2,004	2,316	2,723
3692	Batteries	27,829	29,441	24,880	23,350	29,700
	Other electrical and electronic uses	144	W	W	W	W
38	Instruments and related products:					
382	Measuring and control instruments	3,049	5,671	3,064	2,465	2,842
3843	Dental equipment and supplies	1,779	1,613	1,019	1,597	1,432
	Other instruments and related products	190	253	194	W	W
	Other	790	242	984	1,356	1,404
	Total	58,983	59,244	48,943	49,138	54,602

W Withheld to avoid disclosing company proprietary data; included in "Total."

Source: U.S. Bureau of Mines (Carrico, 1984).

Table 21.4-2
ELEMENTAL MERCURY EMISSION SOURCES IN CALIFORNIA

Firm	City	County	Emission Estimate		kg/yr	kg/yr
			SCAQMD 1b/yr	BAAQMD 1b/yr		
Allied Corporation	Richmond	Contra Costa	-	T	-	T
Allied Corporation		Contra Costa	-	T	-	T
Alta Bates Hospital	Alameda	Alameda	-	T ^a	-	T
American Cyanamid Company	Azusa	Los Angeles	1	-	0.5	-
Ameritone Paint Corporation	Compton	Los Angeles	1	-	0.5	-
Ampex Corporation		San Mateo	-	T	-	T
Atlas Chemical & Mfg. Company	San Diego	San Diego	-	-	-	-
Aurora Pump, Verti-Line Div.	City of Industry	Los Angeles	1	-	0.5	-
Bauer Coating & Chemical Div.	Los Angeles	Los Angeles	1	-	0.5	-
Beckman Instruments, Inc.	Palo Alto	Santa Clara	-	T	-	T
Behr Process Corporation	Santa Ana	Orange	2	-	0.9	-
Best Foods	San Francisco	San Francisco	-	T	-	T
Borg-Warner Corporation	Temecula	Riverside	1	-	0.5	-
Bowman Plating Company, Inc.	Compton	Los Angeles	1	-	0.5	-
Cal-Western Paints, Inc.	Santa Fe Springs	Los Angeles	3	-	1.4	-
California & Hawaiian Sugar	Crockett	Contra Costa	-	T	-	T
Central Contra Costa San. District	Martinez	Contra Costa	-	T	-	T
Central Marin Sanitation District	San Rafael	Marin	-	T	-	T
Chevron Research Company	Richmond	Contra Costa	-	T	-	T
Chevron USA, Inc.	Pittsburg	Contra Costa	-	U	-	U
Chevron USA, Inc.	Pittsburg	Contra Costa	-	T	-	T
Chevron USA, Inc.	San Jose	Santa Clara	-	T	-	T
Chino Basin Mun. Water District	Ontario	San Bernardino	1	-	0.5	-
Clorox Technical Center	Pleasanton	Alameda	-	U ^a	-	U
Commercial Metals Company	San Francisco	San Francisco	-	b	-	b
Delta Diablo Sanitation	Antioch	Contra Costa	-	T	-	T
Drew Refining Company	Berkeley	Alameda	-	U	-	U
Dunn-Edwards Corporation	Los Angeles	Los Angeles	1	-	0.5	-

Table 21.4-2 (Continued)

Firm	City	County	Emission Estimate	
			SCAQMD lb/yr	BAAQMD kg/yr
Exotic Alloys	Los Angeles	Los Angeles	C	-
Ford Aerospace & Communications	Palo Alto	Santa Clara	-	-
Fuller-O'Brien	S. San Francisco	San Mateo	-	-
Genentech, Inc.	S. San Francisco	San Mateo	-	-
Glidden Coatings & Resin	San Francisco	San Francisco	-	-
Globe-Union, Inc.	Fullerton	Orange	1	0.5
GNB Batteries, Inc.	Industry	Los Angeles	1	0.5
H.V. Waddell Company	Burbank	Los Angeles	22	10.0
Hamilton Materials, Inc.	Orange	Orange	1	0.5
Hammond Dental Mfg. Company	Simi Valley	Ventura	-	-
Harold Doc May Subregional	Palo Alto	Santa Clara	-	-
Hartley Company, The	Costa Mesa	Orange	1	0.5
Hewlett-Packard Company	Palo Alto	Santa Clara	-	-
Hewlett-Packard Company	Sunnyvale	Santa Clara	-	-
Hewlett-Packard Company	Palo Alto	Santa Clara	-	-
Hewlett-Packard Company	Santa Rosa	Sonoma	-	-
Hugh J. Resins Company, Inc.	Long Beach	Los Angeles	1	0.5
Kaiser Aerotech	San Leandro	Alameda	-	-
Kaiser Aluminum & Chemical	Pleasanton	Alameda	-	-
Kelly-Moore Paint Company	Ontario	Los Angeles	1	0.5
Lawrence Livermore National Lab.	Livermore	Alameda	-	-
Lockheed Missiles & Space Division	Sunnyvale	Santa Clara	-	-
Long Beach Naval Shipyard	Long Beach	Los Angeles	20	9.1
Los Angeles County San. Dist. 2	Whittier	Los Angeles	1	0.5
Major Paint & Varnish Company	Torrance	Los Angeles	1	0.5
Mare Island Naval Shipyards	Vallejo	Solano	-	-
Martin Metals	Los Angeles	Los Angeles	d	d
Maxwell House	San Leandro	Alameda	-	-

Table 21.4-2 (Continued)

Firm	City	County	Emission Estimate		kg/yr	lb/yr	kg/yr
			SCAQMD	BAAQMD			
Monsanto Company	Martinez	Contra Costa	-	-	-	-	T
Mount Zion Hospital	San Francisco	San Francisco	-	-	-	-	T
National Airmotive Corporation	Oakland	Alameda	-	-	-	-	T
Naval Air Station Alameda	Alameda	Alameda	-	-	-	-	T
New Idria Mining & Chemicals	San Jose	Santa Clara	-	-	-	-	b
Norton & Son of CA, Inc.	Commerce	Los Angeles	1	0.5	0.5	-	-
Old Quaker Paint Co., Inc.	Carson	Los Angeles	1	0.5	0.5	-	-
Pacific Gas & Electric Company	Concord	Contra Costa	-	-	-	-	T
Pacific Gas & Electric Company	Pittsburg	Contra Costa	-	-	-	-	T
Pacific Gas & Electric Company	Antioch	Contra Costa	-	-	-	-	T
Pacific Gas & Electric Company	San Francisco	San Francisco	-	-	-	-	T
Pacific Gas & Electric Company	San Francisco	San Francisco	-	-	-	-	T
Pacific Gas & Electric Company	San Francisco	San Francisco	-	-	-	-	T
PGP Ind., Inc.	Santa Fe Springs	Los Angeles	1	0.5	0.5	-	U
Pyromet Industries	San Carlos	San Mateo	-	-	-	-	T
Raytheon Company	Mountain View	Santa Clara	-	-	-	-	T
Rex Precision Products, Inc.	Gardena	Los Angeles	400	181.4	181.4	-	-
Rockwell International	Anaheim	Orange	1	0.5	0.5	-	-
San Jose State College	San Jose	Santa Clara	-	-	-	-	U
San Mateo, City of	San Mateo	San Mateo	-	-	-	-	T
Shell Chemical Corporation	Carson	Los Angeles	1	0.5	0.5	-	-
Shell Oil Company	Pittsburg	Contra Costa	-	-	-	-	T
Shell Oil Company	Martinez	Contra Costa	-	-	-	-	T
Sinclair Paint Co., Div. of Insilco	Los Angeles	Los Angeles	1	0.5	0.5	-	-
Sonoma Mines, Inc.	Guerneville	Sonoma	-	-	-	-	b
Sparling Instruments Company, Inc.	El Monte	Los Angeles	c	c	c	-	-
SRI International	Menlo Park	San Mateo	-	-	-	-	T
Stanford Linear Accelerator	Menlo Park	San Mateo	-	-	-	-	T

Table 21.4-2 (Continued)

Firm	City	County	Emission Estimate		T
			SCAQMD 1b/yr kg/yr	BAAQMD 1b/yr kg/yr	
Syntex (USA), Inc.	Palo Alto	Santa Clara	-	-	T
Teledyne Controls	Los Angeles	Los Angeles	C	-	-
Todd Shipyards Corporation	San Francisco	San Francisco	-	-	T
Travis AFB	Travis AFB	Solano	-	-	T
TRW Microwave, Inc.	Sunnyvale	Santa Clara	-	-	U
U.S. DOE - Sandia National Lab.	Livermore	Alameda	-	-	T
U.S. Veterans Administration	Livermore	Alameda	-	-	T
U.S. Veterans Administration	San Francisco	San Francisco	-	-	T
Union Chemicals	Rodeo	Contra Costa	-	-	T
Union Oil of CA, S/T Division	Brea	Orange	1	0.5	-
United Airlines, Maintenance	S. San Francisco	San Mateo	-	-	T
United Technologies	San Jose	Santa Clara	-	-	T
US Steel Corporation	Pittsburg	Contra Costa	-	-	T
Varian Associates	Palo Alto	Santa Clara	-	-	T
Vista Paint Corporation	Fullerton	Orange	1	0.5	-
West Contra Costa Sanitation Dist.	Richmond	Contra Costa	-	-	T
Western States Ref. Inc.	Fontana	San Bernardino	7	3.2	-
World Airways, Inc.	Oakland	Alameda	-	-	U
Total			478	216.8	0

Source: Summarized from emissions reported by the South Coast Air Quality Management District (Zwolschner et al., 1983) and the Bay Area Air Quality Management District (Hill, 1985), except where otherwise noted.

^aT = Emissions are 0-0.1 ton/yr; U = Mercury is used but emissions are unknown.

^bSee text.

^cNo consumption in 1984 (Carrico, 1986).

^dMercury cleaning operation; emissions unknown.

21.5 CONSUMER USE AND EMISSIONS

The known sources of potential consumer exposure to mercury are the conventional "D" size battery, which contains 0.01 gram of mercuric chloride, and the "D" size alkaline manganese battery, which contains up to 1.3 grams of elemental mercury. Large size hearing aid batteries contain up to 4 grams of mercuric oxide which is converted to mercury upon discharge (Gosselin, 1984). These products are a source of consumer exposure only if the outer protective cases are broken. Other sources of exposure are dental amalgams, which contain mercury in varying amounts depending upon particular application requirements.

21.6 EMISSION SUMMARY

Estimates of elemental mercury emissions from all identified sources in California are quite uncertain. These emissions, however, are likely to be small. One California mine produces mercury in conjunction with gold. Emissions from associated ore processing are about 0.12 ton/yr. The main indirect sources of mercury include municipal sewage sludge incineration, geothermal power production, and fossil fuel combustion. Releases from these sources are estimated to be 0.07, 0.3 - 0.4, and 0.07 - 0.9 ton/yr, respectively, for a total of 0.4 - 1.4 ton/yr. A lower bound for industrial emissions, which occur mainly from use of mercury in instrument manufacturing, electroplating and used battery reclamation, is about 0.24 ton/yr. Unknown amounts of mercury may be released from use of consumer products and from dental amalgams. It is unlikely that total emissions in the State exceed 2 tons/yr.

21.7 SUMMARY OF AMBIENT CONCENTRATION DATA

Data on ambient atmospheric mercury levels are relatively rare. Mercury has not, for example, been one of the trace elements routinely measured as part of the EPA's National Air Surveillance Network program. Table 21.7-1 summarizes the only California mercury concentration data found in the literature. Data reported by Williston (1968) are for elemental mercury vapor. The high values (25 - 50 ng/m³) measured in the San Francisco

Table 21.7-1
 AMBIENT MERCURY CONCENTRATIONS IN CALIFORNIA
 (Mercury vapor, unless otherwise noted)

Location	Environment	Concentration (ng/m ³)	Reference
Northern California	20 miles offshore, 1000 ft elevation	0.6 - 0.7	Williston, 1968
San Francisco Peninsula			
Winter	Urban and rural	0.5 - 25	Williston, 1968
Summer	Urban and rural	1 - 50	Williston, 1968
San Francisco Bay area	Urban and rural ^a	1.1 - 5.9	John et al., 1973
Stringfellow	Hazardous waste site ^a	0 - 1.8	Shokes and Crabtree; 1986

^aReported as particulate mercury only.

Peninsula occurred in an area overlying the Franciscan formation which, as was discussed in Section 21.3.2, contains relatively high mercury levels. The data reported by John et al. (1973) are for particulate mercury; the percentage of Hg^0 is unknown. In the city of San Francisco, concentrations were 2.8 - 3.6 ng/m^3 . More recently, mercury was measured at the Stringfellow Hazardous Waste Site in Riverside County, as part of a remedial investigation (Shokes and Crabtree, 1986). Hi-vol samplers were placed in Pyrite Canyon just above and below the Site, and 24-hour samples were collected on seven consecutive days. Total particulate mercury concentrations ranged from 0 to 1.8 ng/m^3 . It is not known what fraction of this total comprises elemental mercury. Statistical analysis of the data failed to show a significant contribution of the Stringfellow Site to the observed concentrations.

Mercury has also been measured in several locations outside of California. In three studies reviewed by Rogozen and Hausknecht (1978), urban concentrations of elemental mercury vapor ranged from 0.1 to 40 ng/m^3 . A recent review by Milford and Davidson (1985) identified five studies in which size-differentiated samples of particulate mercury were collected. Total mercury concentrations in those cases ranged from 0.08 to 81 ng/m^3 , and had a geometric mean of 1.9 ng/m^3 . In the studies reviewed by Milford and Davidson, the mass median diameter of the mercury particles was 0.61 μm ; this relatively low value, along with other data presented by these authors, suggest an anthropogenic, high-temperature origin for most of the observed mercury. This is consistent with the nature of the principal indirect sources identified in Section 21.3.

21.8 ATMOSPHERIC CHEMISTRY

Given its high vapor pressure at ambient temperatures, it is reasonable to expect that elemental mercury occurs principally as a vapor or aerosol. Johnson and Braman (1974) found that an average of 4 percent of the total mercury in Tampa Bay, Florida air was in particulate form, about 49 percent was Hg^0 vapor, while 21 and 1 percent of the total was methyl and dimethylmercury, respectively. The species distribution was highly variable, and Johnson and Braman caution that it may not be representative of the general atmospheric mercury distribution.

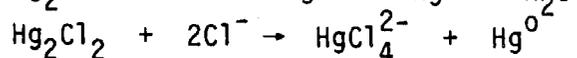
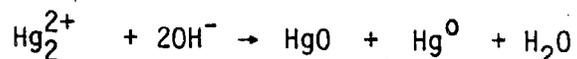
The dynamics of mercury concentrations in ambient air are poorly understood, due to a lack of data (especially on species distribution) and the difficulty of isolating the effects of temperature, ultraviolet radiation, humidity, barometric pressure, wind direction, and sources. The following information is summarized from Burrows et al. (1974), unless otherwise noted.

21.8.1 In-Situ Formation

In the gas phase, organomercurials, such as dimethyl mercury, are decomposed by ultraviolet radiation to elemental mercury and free radicals, as indicated in the following equations:



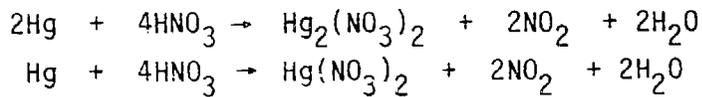
In aqueous phase, mercury (II) derivatives, such as $HgSO_4$, generally do not participate in reactions which lead to formation of elemental mercury. However, a characteristic reaction of all mercury (I) salts, such as mercurous chloride, is disproportionation, i.e. simultaneous oxidation and reduction to a mercury (II) derivative and elemental mercury. Ordinarily the equilibrium constant for the reaction $Hg_2^{2+} \rightarrow Hg^{2+} + Hg^0$ would favor the mercurous form. However, since Hg^{2+} is tied up by reaction with a variety of reagents, the equilibrium is driven to the right. For example, in the reaction with sulfide ion, $Hg_2^{2+} + S^{2-} \rightarrow HgS + Hg^0$. Elemental mercury is also produced by the reaction of mercury (I) with hydroxide and chloride ions:



Whether these reactions occur in solution (e.g. in raindrops) under normal ambient conditions is unknown. However, as mercury (I) compounds are generally quite insoluble in water, it is unlikely that a significant amount of elemental mercury is produced by the aforementioned reactions.

21.8.2 Removal Mechanisms

The reaction of elemental mercury with oxygen at ambient temperatures is very slow in the absence of moisture. Laboratory studies by Takizawa et al. (1975) showed the possibility of photochemical reaction of Hg^0 with acetic acid, acetonitrile and acetaldehyde to form methyl mercury. Given the high solubility of Hg^0 in water, it is possible that many aqueous phase reactions can occur in rain or fog droplets, especially where acids are present. For example, Hg^0 is readily dissolved by nitric acid to form mercurous or mercuric nitrate:



Hg^0 also reacts in hot concentrations of sulfuric acid solutions to form mercurous and mercuric sulfate, although whether this reaction occurs at ambient concentrations and temperatures is uncertain.

Finally, physical entrainment by rainfall is a highly efficient mechanism for removing mercury from the atmosphere (McCarthy et al., 1970).

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22.0
EVALUATION OF NITROBENZENE

22.1 PHYSICAL AND CHEMICAL PROPERTIES

Nitrobenzene is a pale yellow oily liquid. Table 22.1-1 summarizes some of its physical and chemical properties.

22.2 DIRECT PRODUCTION IN CALIFORNIA

In 1978, five companies produced nitrobenzene at seven locations. The production facilities are located along the Gulf Coast, in New Jersey, and in West Virginia. No production took place in California.

22.3 INDIRECT PRODUCTION AND EMISSIONS IN CALIFORNIA

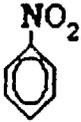
As discussed in Section 22.8, nitrobenzene may form in the atmosphere by the OH-initiated photooxidation of benzene. Other indirect mechanisms for the production of nitrobenzene are not presently known.

22.4 INDUSTRIAL USE AND EMISSIONS

In 1978, 98 percent (833 MM lb) of domestic nitrobenzene production was used captively for aniline; the remaining two percent (12.75 MM lb) was used as a solvent for cellulose ethers, and as an intermediate in the manufacture of dinitrobenzenes and dichloranilines (4.5 MM lb)(SAI, 1980; Dorigan and Hushon, 1976). The use of nitrobenzene as a selective solvent in the petroleum industry has also been reported (SAI, 1980). However, according to two major California refineries contacted by SAIC, the compound is not used in oil refining in the State (Wilkniss, 1986; Williams, 1986).

References which may be outdated, and have not been confirmed, indicate that nitrobenzene may also be used in metal polishes, soaps, shoe blacking, perfume, as a dye intermediate and leather dressing, and for refining lubricating oils (SRI, 1974; Merck Index, 1976).

Table 22.1-1
 CHEMICAL DATA SUMMARY FOR NITROBENZENE

Property	Value for Nitrobenzene
CAS Registry No.	98-95-3
Synonyms	Nitrobenzol, mononitrobenzene, oil of mirbane
Molecular Weight	123.11
Molecular Formula	$C_6H_5NO_2$
Molecular Structure	
Physical State at STP	Solid/oily liquid, colorless, volatile oil
Boiling Point	210.8°C at 760 mm
Melting Point	5.7°C
Specific Gravity	1.2037 at 20°C/4°C
Vapor Pressure	0.284 mm at 25°C
Vapor Density (air=1)	4.25
Solubility	Slightly soluble (8 g/L at 80°C)
Log Partition Coefficient (octanol/H ₂ O)	1.88
Henry's Law Constant	

Source: SAI (1980).

In a recent evaluation of potential toxic air pollutant emissions in the San Francisco Bay area, the Bay Area Air Quality Management District identified 13 facilities where nitrobenzene is handled (Hill, 1985). These are shown in Table 21.4-1. Information for estimating emissions from these sources was not available. Most of the facilities produce electronic equipment.

22.5 CONSUMER USE AND EMISSIONS

Consumers may be exposed to nitrobenzene through a variety of products such as shoe polish, floor polish, and leather dressings. A literature and formulary search found nitrobenzene listed as a potential ingredient for leather conditioners, shoe polishes, shoe dyes and floor cleaners. No detailed information such as concentration of nitrobenzene in the product or quantities of production for the products could be located. These formularies are not updated frequently and ingredient lists may be dated. We have not been able to confirm the presence or absence of nitrobenzene in these products.

22.6 EMISSION SUMMARY

Nitrobenzene is not directly produced in California, but may form in the atmosphere in the presence of benzene. Its industrial use in the state is unknown but does not appear to be major. Consumers may be exposed to small amounts of nitrobenzene from a variety of products such as shoe polish, floor polish, metal polish, some soaps, perfume, and leather dressings.

22.7 SUMMARY OF AMBIENT CONCENTRATION DATA

No ambient concentration data are available for nitrobenzene in California. Bozzelli et al. (1979, 1980) have measured ambient levels of nitrobenzene at nine locations in New Jersey. Pellizzari (1977, 1978) also measured nitrobenzene at several sites in New Jersey and one site each in New York and Louisiana. The combined data base includes mean values of up to 0.37 and maxima of 2.8 ppb (Newark, NJ).

Table 22.4-1
 NITROBENZENE EMISSIONS IN THE SAN FRANCISCO BAY AREA

Source	City	Emissions (tons/yr)
<u>Alameda County</u>		
Clorox Technical Center	Pleasanton	U
DOE - Sandia National Laboratory	Livermore	T
Lawrence Livermore National Laboratory	Livermore	U
<u>San Francisco County</u>		
U.S. Army (Presidio)	San Francisco	T
<u>Santa Clara County</u>		
Beckman Instruments, Inc.	Palo Alto	T
General Electric Company	San Jose	T
Hewlett-Packard Company	Palo Alto	T
Siemens Optoelectronics	Cupertino	T
Syntex (USA) Inc.	Palo Alto	T
Western Spray Painting	Santa Clara	U
<u>Sonoma County</u>		
Hewlett-Packard Company	Santa Rosa	T
<u>San Mateo County</u>		
Ampex Corporation		T
SRI International	Menlo Park	T

Source: Bay Area Air Quality Management District (Hill, 1985).

^aT = 0-0.1 tons/yr; U = Nitrobenzene is handled but emissions cannot be estimated from available information.

22.8 ATMOSPHERIC CHEMISTRY

22.8.1 In-Situ Formation

The OH-initiated photooxidation of benzene yields nitrobenzene as a major reaction product. The reaction is slow, $k_{OH} = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, and involves OH addition, as is shown in Figure 22.8-1. The benzene-OH adduct may react with NO_2 to form nitrobenzene, with O_2 (abstraction) to form phenol, and with O_2 (addition) to form ring-opening products. According to Bandow et al. (1985), phenol is the major product, followed by nitrobenzene, whose yield is about half that of phenol. These two compounds account for about 80 percent of the total reacted toluene, the remaining 20 percent being accounted for by ring-opening products, including formaldehyde, formic acid, maleic anhydride, and glyoxal (Bandow et al., 1985).

Concentrations of benzene in the Los Angeles area are in the range 5-30 ppb (e.g. Singh et al., 1981; Grosjean and Fung, 1984; Shikiya et al., 1984). For typical values of benzene (10 ppb) and OH (10^{-7} ppm), and with k_{OH} about $1.8 \times 10^3 \text{ ppm}^{-1} \text{ min}^{-1}$, the rate of benzene removal by reaction with OH is 0.1 ppb per hour. Assuming further from Bandow et al. (1985) a nitrobenzene yield of 22 percent, the formation rate of nitrobenzene is about 0.022 ppb/hour. Since nitrobenzene in turn reacts with OH about 10 to 20 times slower than does benzene (see Section 22.8.2), only a small fraction of the nitrobenzene formed will be removed. Thus, up to about 0.2 ppb of nitrobenzene may form in a day in the Los Angeles atmosphere.

22.8.2 Removal Processes

Photolysis, reaction with O_3 , and reaction with NO_3 are of negligible importance. Removal of nitrobenzene by reaction with OH is very slow. The rate constant we estimated from structure-reactivity relationship (see Chapter 3) is about $6.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The experimental value obtained by Zetsch (as reported by Dilling, 1986) is about $1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Nitrobenzene is therefore expected to be a long-lived contaminant in urban air.

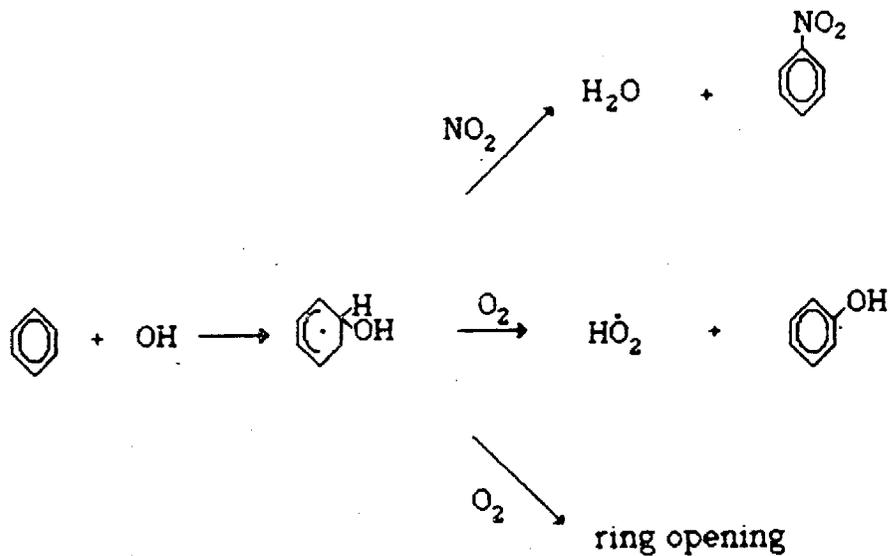


Figure 22.8-1. OH-Benzene Reaction.

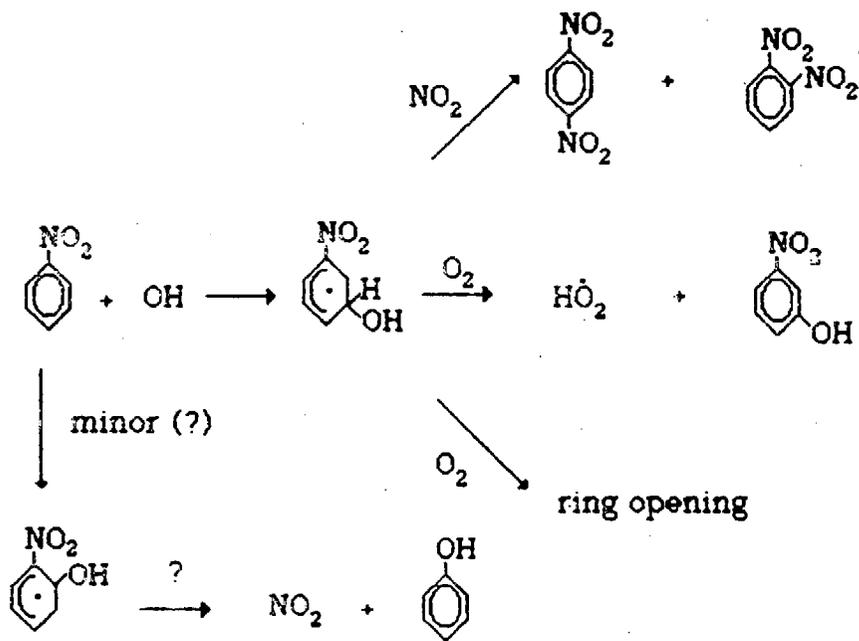


Figure 22.8-2. OH-Nitrobenzene Reaction.

Products of the OH-initiated oxidation of nitrobenzene have not been studied. A tentative mechanism is outlined in Figure 22.8-2 and includes the major features of the OH-aromatic hydrocarbon reaction mechanism. Expected products are 3-nitrophenol, dinitrobenzene (2 isomers), and aliphatic dicarbonyls following aromatic ring opening of the nitrobenzene-OH-O₂ adduct. Another possible pathway may involve OH addition at the NO₂-bearing carbon followed by elimination of NO₂ to form phenol.

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